



University
of Glasgow

<https://theses.gla.ac.uk/>

Theses Digitisation:

<https://www.gla.ac.uk/myglasgow/research/enlighten/theses/digitisation/>

This is a digitised version of the original print thesis.

Copyright and moral rights for this work are retained by the author

A copy can be downloaded for personal non-commercial research or study, without prior permission or charge

This work cannot be reproduced or quoted extensively from without first obtaining permission in writing from the author

The content must not be changed in any way or sold commercially in any format or medium without the formal permission of the author

When referring to this work, full bibliographic details including the author, title, awarding institution and date of the thesis must be given

Enlighten: Theses

<https://theses.gla.ac.uk/>
research-enlighten@glasgow.ac.uk

STUDIES IN THE LIGHT FADING OF DYES

by

DEVENDRA PRATAP JHARI

A THESIS

Submitted to the

UNIVERSITY OF GLASGOW

in accordance with the regulations

governing the award of the

DEGREE OF DOCTOR OF PHILOSOPHY

IN THE FACULTY OF SCIENCE.

Surface Chemistry and Dyeing Research Laboratory,
Department of Pure and Applied Chemistry,
University of Strathclyde,
GLASGOW, G.1.

OCTOBER, 1966

ProQuest Number: 10646020

All rights reserved

INFORMATION TO ALL USERS

The quality of this reproduction is dependent upon the quality of the copy submitted.

In the unlikely event that the author did not send a complete manuscript and there are missing pages, these will be noted. Also, if material had to be removed, a note will indicate the deletion.



ProQuest 10646020

Published by ProQuest LLC (2017). Copyright of the Dissertation is held by the Author.

All rights reserved.

This work is protected against unauthorized copying under Title 17, United States Code
Microform Edition © ProQuest LLC.

ProQuest LLC.
789 East Eisenhower Parkway
P.O. Box 1346
Ann Arbor, MI 48106 – 1346

Acknowledgements

The author wishes to express his gratitude and sincere thanks to Dr. G.H. Giles for his encouragements and guidance throughout the present investigation and to Professor P.D. Ritchie, F.R.S.E., for the interest he has shown in this work.

Thanks are also due to Dr. G. Weaver for his help in obtaining the electron micrographs and to Dr. N. Peacock for x-ray photographs, Dr. H.M. Elder for specific gravity measurements, and to Mr. D.B.F. McAndrew for his help in general. The author also wishes to thank Ian Mackin and J. & P. Goats Ltd., and P.R. Dawson and I.C.I. Ltd. Dyestuffs Division, for their help in testing the samples.

Preface

The aim of the whole investigation was to study a variety of factors which may have an influence in improving the light fastness of dyed fibres. These factors include the concentration and the physical state of the dye, and its binding with the fibre; the internal crystallinity of the fibre and its external roughness; the humidity of the atmosphere; and the intensity of the light. In addition the effect of some variables in testing methods were examined.

Most of these factors have been studied before, either here or elsewhere, but a great deal more information about them is required before a satisfactory picture of the dye fading process in fibres can be given.

Summary

The work includes the use of a variety of means of detecting aggregates of dye in fibres and films. These include electron microscopy and studies of reaction rate.

Mainly this work was directed towards elucidating the causes of the improvement in fastness obtained when some reactive dyes become fixed (i.e. covalently bonded) to cellulose.

The effect of other substituents such as glucose and methanol, which are similar to cellulose in reaction with the dye forming other linkages, have been studied.

The light fastness of fixed dyeings on both Cellophane film and "gel"-Cellophane (i.e. undried material) was higher than that of the unfixed dyeings.

X-ray technique ^{like} ~~also~~ did not show any presence of dye aggregates. But the aggregates were detected with the aid of electron microscopy, in fixed dyeings on cellulose films. Their detection in unfixed dyeings on cellulose was not possible as the dye bleeds out in water, before the film is taken on the grid for electron micrograph.

The absence of any dichroic effect in the fixed and unfixed dyed films suggested the presence of aggregates and the absence of orientation of dye molecules.

Fading of reactive dyes on different substrates e.g. bleached cotton, mercerised cotton and viscose rayon showed an increase in light

fastness with the porosity of the material, i.e. viscose rayon the most amorphous of these fibres gives the highest light fastness.

The general conclusion is that the light fastness of reactive dyes is possibly unaffected by the dye-fibre bonds and is related to its aggregation in the substrate.

Among other aspects of light fading which were studied are the effect of roughness of fibre surface, of alternate irradiation and storage in the dark of the dye, of various methods of mounting films for exposure, with or without glass support, of the theoretical aspects of the effect of shade depth on fading rate, and of the influence of moisture diffusion rate in the substrate.

C O N T E N T S

	<u>Page</u>
<u>GENERAL INTRODUCTION</u>	1.
Evidence of oxidation and reduction in fading	1.
The effect of light intensity on fading	2.
Photochemistry of fading	2.
Conductivity and its effect on fading mechanism of dye	6.
Non-radiant energy transition	10.
The effect of light of different wave bands on fading	11.
Environmental effects on fading	12.
Effect of dye concentration on fading	12.
Characteristic fastness grade	14.
Relation between physical state of dye and its fading	16.
Detection of aggregates by electron microscopy	18.
Qualitative estimation of aggregation	20.
Effect of substrates on fading	22.
Effect of temperature and moisture on fading	26.
<u>INTRODUCTION TO THE PRESENT WORK</u>	27.
Effect of dye-fibre bond strength on the light fastness of reactive dyes	28.
Chemistry of the reactive dyes	29.
(a) Cyanuric chloride residues	29.
Reaction with cellulose	32.

	<u>Page</u>
Evidence for a chemical reaction with the fibre	35.
Evidence for the site of reaction in cellulose	38.
Accepted conformation of the cellulose molecule	39.
(b) Based on vinyl sulphone	40.
(c) Based on tetrachloropyrimidine	42.
(d) Based on an epoxy group	43.
Previous work	44.
Effect on direct dyed Cellophane fading rates of alternating irradiation and storage in the dark	49.
Difference in fading of direct dyes in glass slides and in open exposure	50.
Effect of external roughness of the film on dye fading	50.
The results of Weissbein and Govon's tests correlated with fading rate curves	50.
The y/x - band ratio of different dyes in different media	51.
Effect of dye layer thickness on fading	51.
Fading of dyes in oriented and disoriented polyester films	52.
 <u>EXPERIMENTAL</u>	
Sources of irradiation	54.
Measurement of fading	55.
The calculation of relative fading rate from fading curves	56.

	<u>Page</u>
Mounting and exposure of dyed films	57.
Dyeing of Cellophane and gel-Cellophane films with reactive dyes	57.
Procion dyes	59.
Benzol dyes on Cellophane	61.
Cibacron dyes on Cellophane	62.
Levafix dyes	63.
Drimarone dyes	63.
Dyeing of mercerised and unmercerised cotton and viscose rayon yarn with Levafix Brilliant Blue E-B	64.
Dyeing of cotton poplin by Thomasol process	64.
Preparation of Cellofas A films (methyl ethyl cellulose)	65.
The light fastness of Procion dyes with and with- out glucose	66.
The light fastness of reactive and direct dyes dyed with glucose at pH 10.5 and 5.0	66.
Light fastness of hydrolysed and unhydrolysed reactive dyes	67.
Reacting methyl alcohol with reactive dye before dyeing Cellophane	67.
Effect of sodium hydroxide on direct dyes	68.
Difference in light fading of direct dyes (having a free chlorine atom at the triazine ring) with and without alkali	68.
The light fastness of unfixed dyeings after different times of washing	69.
Irradiation by mercury vapour lamp of two dyes having the same base but an additional triazine ring attached in one (reactive dye)	69

	<u>Page</u>
Fluidity measurements of fixed dyed Cellophane film before and after fading	70.
Fading of mercerised cotton, unmercerised cotton and viscose rayon yarn dyed fixed and unfixed, tested by xenotest and fadeometer	70.
Detection of dye aggregates by x-ray photography	70.
Qualitative examination of dichroic effect in fixed and unfixed dyed Cellophane films	71.
Irradiation of dye solutions by mercury vapour lamp	71.
Electron microscopy	71.
Section cutting by microtome of the dyed Cellophane film	71.
Making very thin cellulose film for electron microscope	72.
Preparation of cellulose triacetate film	73.
Preparation of glass slides	73.
Casting of film	74.
Conversion of cellulose triacetate to cellulose film	74.
Dyeing of films for the electron micrograph	75.
Preparation of polyester films for electron micrographs	75.
Difference in fading of direct dyes in glass slides and in open exposure	76.
Fading of direct dyes having glass slide and metal slide only on one side in each case	76.
Fading of direct dyes in glass slides with and without an air gap in between the two slides	77.
Difference in temperature rise between glass and metal slides on exposure to the lamp	77.

Preparation of gelatin films	77.
Gelatin film having one or two rough surfaces	78.
Films having different grades of roughness	78.
Dyeing and drawing the fading rate curves of direct dyes	78.
Fading of Chlorazol Sky Blue FF and Duranol Violet 2R 300 on Cellophane and polyester films	79.
Preparation of polyester film	80.
Disorienting polyester film by boiling	80.
Fading under dry and wet conditions	80.
Uptake of moisture by oriented and disoriented polyester film	81.
Fading of Dispersol Orange A150 Powder on cellulose triacetate, sandwiched between polyester and cellulose triacetate films separately	81.
 <u>DISCUSSION</u>	
Effect of dye-fibre bond strength on the light fastness of reactive dyes	83.
Effect on direct dyed Cellophane fading rates of alternating irradiation and storage in the dark	90.
Difference in fading of direct dyes in glass slides and in open exposures	91.
Effect of external roughness of the film on dye fading	93.
Weissbein and Coven's tests correlated with fading rate curves	94.
The y/x bond ratio of different dyes in different media	95.
The effect of dye layer thickness on fading	96.

	<u>Page</u>
Fading of dyes in oriented and disoriented polyester film	98.
<u>CONCLUSIONS</u>	100.
<u>REFERENCES</u>	101.
<u>TABLES</u>	
<u>FIGURES</u>	
<u>APPENDIX</u>	

GENERAL INTRODUCTION

The problem of light fastness of dyes becomes more important with the invention of new fibres and dyes for them. But the light fastness of a dye is not an absolute property and depends upon the medium to which it is applied and how it is applied. The other factors which affect the light fastness of a dye include the presence of moisture, air, and impurities present therein, the nature, and the intensity of the illumination, the physical state of the dye and the substrate, etc.

Evidence of Oxidation & Reduction in Fading

Cumming et al.⁽¹⁾ concluded that fading is normally an oxidation of dye on a non-protein but a reduction on protein substrates and that probably non-protein substrates do not take part in the initial fading reaction, but protein substrates do so. The chemical structure of the dye also of course plays its part in its fading reactions; e.g. the symmetry of substitution⁽²⁾, the nature of the substituent groups, and their position. It has been shown by several authors that the light fastness of azo dyes on cellulose is increased by substituent groups e.g. p-nitro- and p-chloro- groups, which cause resistance to oxidation.⁽³⁾ Filippychov⁽⁴⁾ noted that straight chain polyazo dyes with more than three azo groups, and those with separated conjugated systems (e.g. separated by a cyanuric⁵ ring, etc.), among other types, tend to have good fastness.

The Effect of Light Intensity on Fading

The effect of light intensity and time on fading was studied by Imori and Kitaoka⁽⁵⁾ and they found an inverse relation between light intensity and time required for a given fade in dyed cellulose acetate films exposed to mercury vapour light. Gebhard,^(6,7) claimed that there is a threshold light intensity for every dye below which no fading occurs, but the conclusions drawn by the A.A.T.C.C.⁽⁸⁾ were that there is no threshold light intensity below which fading does not occur, and the amount of dye faded is probably proportional to the illuminant intensity.

A linear relation between the logarithm of light intensity and the (degree) of fading expressed in precise colorimetric terms, with no threshold value of intensity was shown by Bedford.⁽⁹⁾

Photochemistry of fading

Fading is a photochemical change and is governed by three laws :

(i) the Grothus-Draper law, which states that only radiations which are absorbed by the reacting system are effective in producing chemical change and (ii) the Stark-Einstein law, which states that each molecule taking part in a chemical reaction induced by exposure to light absorbs one quantum of the radiation. (iii) the Beer-Lambert absorption law -

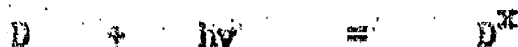
The absorption of a monochromatic beam of light by a homogeneous absorbing system is described well by the familiar combined Beer-Lambert law. It is commonly employed in photochemical studies :-

$$\frac{I}{I_0} = 10^{-\epsilon cl}$$

Where I_0 = light energy (or number of quanta) of strictly monochromatic light incident per unit of time at the front of a column of a single absorbing species of concentration C , moles/liter; I is the energy per unit time transmitted through the column of material, l cm. in length and ϵ (liters/moles/cm), the molar extinction coefficient, is a constant for a given pure absorbing species at a given wavelength and is a measure of the probability that the quantum-molecule interaction will lead to absorption of the quantum.

The above relationship is derived readily by assuming that the probability of light absorption is simply proportional to the number of bimolecular encounters between light quanta and absorbing molecules.

The photochemical changes follow molecular excitation by absorption of light energy normally from the visual or ultra-violet regions of the spectrum ($\lambda = \text{Ca. } 2000\text{--}7000 \text{ \AA}^0$). The vibrational and rotational energy of the molecule or its electron system is increased to higher energy levels by the absorption of radiation falling upon it.



($h\nu$ represents one quantum of radiation with frequency ν)

Bown⁽¹⁰⁾ pointed out that the excited singlet level may pass on to a triplet level which may be chemically more reactive and have a much longer mean life time than the excited singlet level. Further, he suggested that the very low quantum yield of a photoreaction such as that of dye fading (10^{-6}) may quite possibly be due to the low probability of such a "forbidden" transition taking place rather than to the

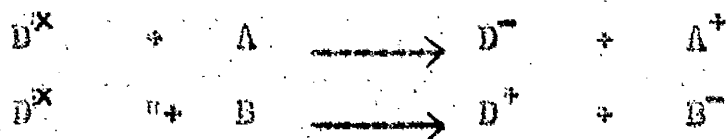
very short life of the excited singlet level. Lewis⁽¹¹⁾ has also considered the direct transition from singlet ground level to triplet level.

The excited molecule is unstable and thus may change in one or another of the following ways⁽¹²⁾ :-

- (i) transfer all or some of the energy it has acquired to other molecule^c or
- (ii) become an ion through an electron transfer process; or
- (iii) split into two fragments or radicals, in which the total change is zero; or
- (iv) react in its excited state with another molecule; or
- (v) re-emit the absorbed quantum as fluorescence or phosphorescence.

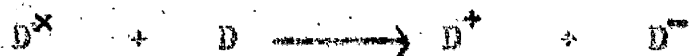
A number of formal schemes have been suggested by Bowen⁽¹⁰⁾, to explain electron transfer reactions.

The dye molecule D^* , either in the excited singlet level or in the triplet level, may react with either reducing agent A and/or oxidising agent B to give the corresponding reduced D^- or oxidised D^+ dye-radical ion, thus :-



The existence of free radicals in the form of dye molecules rather than H atoms or OH radicals has been demonstrated by Hillson and Rideal (13) who detected their presence by the polymerisation of methyl methacrylate in the dye solution, on illumination, and to some extent even in the dark.

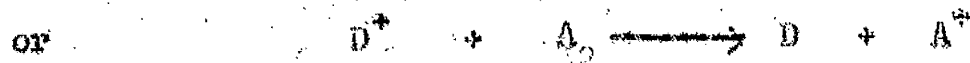
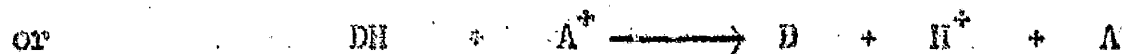
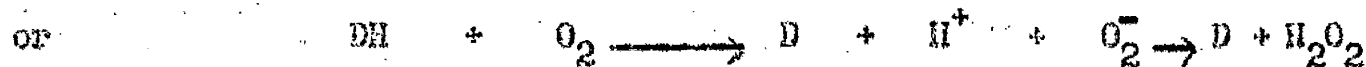
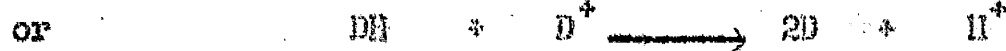
A dismutation reaction may occur,



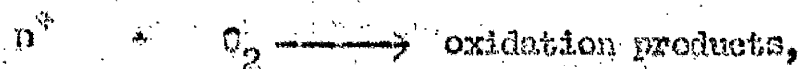
and the ions so formed may react further to give a semiquinone:



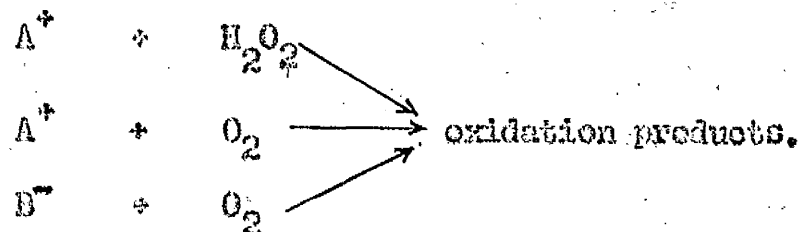
or, reformation of the dye, either



Destruction of the dye may take place with the formation of oxidation products,



and the ions formed other than dye ions may also react with each other to form further stable oxidation products, thus :-



Two or more of these reactions can take place simultaneously, depending on extraneous conditions such as the nature of the substrate, leading, as in the case of the more complicated dyes, to a complexity of final fading products. The successful separation and identification of these fading products would not, in all probability, elucidate entirely the mechanism of fading, as any attempt to name the unstable intermediates could only be hypothetical.

Conductivity and its effect on fading

Mechanism of dye

Semiconductors are a class of solids whose resistivities are intermediate between those of typical metals and the typical insulators but unlike metals the conductivities of these substances increases with increase of temperature. This property of semiconductors is called semiconductivity.

The substances such as zinc sulphide which thus become better conductors of electricity also start conducting when exposed to light; this phenomenon is called photoconductivity. Some dyes also have now been found to have photoconducting properties, and this property is conveniently examined in thin deposited films of solid dye.

It is believed that electrons contributing to semiconductivity and photoconductivity are in different levels, in order to account for the connection of the latter with the photobleaching process. Photo-bleaching is considered to occur by a free-radical mechanism. (14)

The conductivity of the dye films in the dark increases with the temperature, from room temperature to 90°C. But on illumination of a semiconductive dye film, the conductivity rises over a few minutes and acquires a limiting value. When the light was cut off, a slow decay to the original dark conductivity was found⁽¹⁵⁾.

The larger molecules have increased numbers of delocalised π -electrons that contribute to the conductivity. The theory of the conductivity of organic solids put forward by Eley and Parfitt⁽¹⁶⁾ is based on a molecular-barrier model, the π -electrons in molecular orbitals may be excited from the highest filled $n/2$ level (where n is the number of π -electrons in the molecule) to the $(n/2 + 1)$ level. Quantum-mechanical tunnelling in an applied potential field then causes the excited electron to pass through the potential barrier to a neighbouring molecule.

A radiationless transition to the triplet state by a "spin-flip" is possible from one of these levels, at the point where the potential energy curves of the excited singlet and of the triplet states intersect. As suggested by Nelson⁽¹⁷⁾ the absorption of light energy ($h\nu_0$) raises electrons from the ground state to trapping levels, and a further thermal activation energy E_{ph} is then needed to raise the electrons to conductive states. It has been demonstrated that when E_{ph} increases the light fastness rating is also increased⁽¹⁴⁾, in the case of three dyes, closely related chemically (Table 2).

There is evidence, from electron spin resonance measurements, for

the existence of free radicals in photoconducting dye films⁽¹⁸⁾.

Patterson and Pilling⁽¹⁴⁾ suggested that the primary process in photoconduction is the production of excitons by the absorption of light and that these are the first energy carriers. The excitons can only travel a short distance through the crystal lattice before dissociation into a positive hole and an electron at a trapping site. However, the hole and electron need not necessarily be trapped by the same dye molecule; after the trapping of the hole, the electron may diffuse further and act as a charge carrier. These authors suggest that some dyes improve their light fastness in a polar medium due to the excitons being readily trapped and destroyed by the ionic lattice, preventing the subsequent stages leading to fading of the dye. They give a similar explanation for the better light fastness found in acid dyes on anodized aluminium. But in this laboratory⁽¹⁹⁾ Detye showed that the good light fastness of acid dyes on anodized aluminium is due to the "sealing" process given to the films after dyeing, by which boiling water causes the blockage of pores in the film by growth of aluminium hydroxide. When an increase in light fastness is found with a dye associated with a non-polar substrate, Patterson and Pilling suggest that the cause is the insulating effect of the non-polar substrate. They state that when the ratings of a given disperse dye on polyacrylonitrile, polyester, polyamide and secondary acetate fibres, respectively, are examined, the light fastness on the later fibres in this series is lower than on the earlier ones. The electrical resistance of the fibres falls in a similar manner, though an overlapping range of values is given for the

fibres⁽²⁰⁾.

Due to several weak points in these hypotheses it cannot be generalised for all dye-fibre systems. The following objections can be listed against it.

(a) The experiments were made on solid deposited films of dye which is in quite a different physical state compared with the dye in the fibre. The work done in this laboratory (Fig.1 and Table I)^{*} - by others and by the author (Fig.2) - definitely suggests that the dye used by them (acid wool dyes) is present in protein fibres at least partly as mono disperse molecules, and if so, then the photoconducting mechanism will differ from that they observed in solid dye. If however it is accepted that the dye is present in the form of particles or aggregates in the fibre, so as to make their suggested mechanism applicable, then surely the geometrical characteristics of the particles will be more important in determining the fading rate, than the photoconducting properties of these particles of dye.

(b) Only three dyes of similar basic chemical structure were tested. The correlation between photoconducting properties and the fastness of the dyes as reported by them, may not be applicable to other dyes having different chemical structures. Cumming et al⁽¹⁾ found that dyes having the same basic constitution and with only small variations in substitution

* See page 19

(b) (Cont'd)

show a correlation between chemical properties or structure and light fastness.

(c) It is incorrect to assume that all dyes are ranked in the same fastness order on the series of substrates quoted.

This is not always true: fastness varies greatly with concentration in the fibre and its mode of variation is different for different dyes on fibres.

The dyes used by Patterson and Pilling are the ones used on wool as light fastness standards 1, 2, and 3. Their formulae (Table 2) show that they have much the same structure. With these variations among them, their light fastness rises with the increase in electron density on the central carbon at least ^{perhaps} with the first two ⁽²¹⁾ i.e. with the increase in resistance to reduction. This agrees with the findings of Gunning et. al ⁽¹⁾ that for dyes on wool fading involves reduction of dye. It is certainly interesting that these dyes when tested in quite a different physical state and environment from those in which they exist in a wool-fibre, have the same rating; and the fact suggests that the same underlying cause operates in both situations.

Non-radiant energy transition

On irradiation with light a dye molecule may start radiating fluorescent light of a certain frequency. This in turn passes its energy to another molecule which keeps on oscillating even if the first one has ceased to oscillate. This is due to the fact that the non-

radiant oscillation energy has been transferred from the first to the second molecule. But this transition is possible only if the distance between the two molecules is less than $100\text{\AA}^{(22)}$, failing which the first molecule fluoresces and there is no non-radiant transition.

The effect of light of different wave bands on fading.

Iuszcak and Zukriegel⁽²³⁾ found, that there is a relation between fastness grade and the wavelength of a characteristic absorption waveband of the dye in the ultra-violet region; the shorter is the wavelength the higher is the fastness rating and fading is caused mainly by an absorbed waveband with a fairly definite upper boundary at about twice the characteristic wavelength. Beyond this boundary absorbed light is almost inactive.

The most effective spectral region for some dyes on synthetic fibres lies between 3500 and 4250 \AA , according to Kobsa and Me^erov⁽²⁴⁾.

The far-ultraviolet radiation(2537\AA°) has energy sufficient enough⁽²⁴⁾ to rupture various covalent bonds (e.g. carbon-carbon, carbon-oxygen), whereas visible and near-ultraviolet radiation does not. It is suggested that in the first place, with the effect of these radiations, free radicals are produced in the cellulose molecule. It was suggested⁽²⁴⁾ that on irradiation of wood cellulose, there are two modes of primary fission of the cellulose chain: (a) between C_1 of the glucose unit and the attached glycosidic oxygen atom and (b) between C_1 and C_2 of the glucose unit. Deelik and Hamilton, quoted by Egerton⁽²⁵⁾

suggested that the acetal group at C_1 acts as a weak chromophore and thus initiates photolysis of the cellulose. Various gaseous products (hydrogen, carbon monoxide, and carbon dioxide) have been identified in the degradation of cellulose in vacuum by a 2537\AA radiation.

Environmental effects on fading

Substances external to the fibre which can affect the fading of dyes include oxygen⁽²⁶⁾; acidic impurities, which give a discoloration known as "gas fume fading"^(27,28) and smog⁽²⁹⁾. It has been established that dyes on cellulose acetate are more susceptible to nitrogen oxides than they are on wool⁽³⁰⁾. The nitrogen oxides (higher oxides mainly) react with basic groups in the dye and the ease of reaction increases with basicity thus: $\text{NH Ar} < \text{NH alk} < \text{NH}_2$. Hydroxy groups do not appear to react. The primary amino-groups form a diazo^{nium}-nitrate and the secondary ones a N-nitrosamine. Sulphur dioxide modifies the action of nitrogen oxides (e.g. N-nitrosamine formation is retarded). The blue dyes are the most susceptible to gas-fume fading, the reason for this is that amino-groups in the molecule are required to shift the light absorption band towards long wavelengths, i.e. to give a blue shade.

Effect of dye concentration on fading

Barker, Hirst, and Lambert⁽³¹⁾ found that the actual loss of colour is independent of the amount of dye present. According to them a given amount of absorbed energy can cause the destruction of only the same amount of dye, whatever amount may originally be present. This, of

course is the condition normally obtained in photochemical reactions when the whole of the active radiation is absorbed, the number of molecules decomposed then becoming proportional to the time of exposure. This is known as a reaction mechanism of zero order, so that if the dyed fabric absorbs the whole of the active radiation, the relationship established by Barker, Hirst and Lambert is normal.

An empirical relationship between fading and the square root of the exposure time was found by Gunliffe and Lambert⁽³²⁾. As a measure of degree of fading they used the percentage decrease in the distance of the point on the colour-chart, representing the dyed pattern, from that representing the undyed material. It was discovered by them that this point in most cases moved steadily towards "white" with the progress of fading. They obtained the relation: $F = \underline{a}\sqrt{t} + \underline{b}$ - - - (i), where, F = amount of dye faded and \underline{a} and \underline{b} are constants; this applied to the stages of fading up to 60% and the relation,

$$F = C \log \frac{a}{b} + d \quad - \quad - \quad - \quad - \quad (ii)$$

where, C and $\frac{a}{b}$ are constants, applied also to the fading at about 25% loss. In addition they found empirical equations of other types to hold over a limited range. They argue, that since photochemical changes always vary in reaction order between the limit of zero (for the total absorption of light)

$$\text{where, } F = kt \quad - \quad - \quad - \quad - \quad (iii)$$

and unity (for partial light absorption)

$$\text{where, } F = e^{-kt} \quad - \quad - \quad - \quad - \quad (iv)$$

then the dye fading should also vary in reaction order between these

limits, passing from zero to first order as the dye disappears. With most dyes they found equation (iii) to hold in the early stages of fading and in the later stages the exponential law was found to apply as predicted. The \sqrt{t} relationship (equation (1) for medium values of t was shown to be a consequence of the exponential law. Their results do not seem to agree with the very large number reported by workers in this laboratory over a long period, whereby an initial first-order fade may be followed by one of zero order, but never or very seldom is the opposite sequence found.

An empirical linear relation between fading and the initial dye concentration was also shown by Cunliffe and Lambert.

$$F = f \log C_0 + g \quad \text{--- (v)}$$

where f and g are constants, the slope f of the curve varying from one dye to another.

They combined their empirical equations in one general expression showing the relation between original dye concentration, time of exposure and extent of fade :-

$$F_t = 100 (1 - e^{-t (f \log C_0 + g)}) \quad \text{--- (vi)}$$

Sommer⁽³³⁾ also noticed an empirical linear relation between amount of fading and square root of exposure time.

Characteristic fastness grade

Eaton, Giles and Gordon⁽³⁴⁾ found a linear relation between light fastness grade number and logarithm of dye concentration on the fibre. The lines so obtained were termed "characteristic fastness grade" (CFG)

curves⁽³⁵⁾. The light fastness grades represent a geometrically graded series of patterns of increasing light fastness. The test sample is given the grade number of the standard which shows the same degree of fade under equal exposure conditions, the fading being judged in the early stages. If it is to be assumed that the percentage colour loss for a pattern to be judged "faded" is the same, no matter what the grade number, then it follows that there should be a linear relation between the logarithm of the time required (t_F) to produce a given fixed percentage loss of any dye and the logarithm of its initial concentration (C_0); i.e.

$$\log t_F = a^1 \log C_0 + b^1 \quad \text{--- (vii)}$$

where a^1 and b^1 are constants and thus the linearity of the characteristic fading grade curves is explained.

Dexter et al.⁽³⁶⁾ first described the method of plotting the logarithm of the time (t_F) required for a given percentage loss of dye by fading (conveniently 10%) against the logarithm of the initial dye concentration (C_0). The linear curves so obtained (t_F curves) were shown by Giles to be equivalent to the C.F.G. curves, since t_F is equivalent to a fastness grade on a geometrical scale. The position and slope of these curves depends upon the change in size distribution of dye particles with concentration rather than on the size of the largest ones. A dye which tends to form a collection of particles of many different sizes will give a steeper curve than one forming some of a more uniform size. The later dye could be said to be more aggregated, yet at higher shade depths, if the curves cross, it would be the less

fast.

Eaton et al⁽³⁴⁾ found that each dye/fibre system has a characteristic mean slope, about which the slopes for the individual dyes in the system may be grouped and the magnitude of the slope can be shown to be a measure of the "apparent reaction order" of fading.

Relation between physical state of dye
and its fading

The fastness of a dye increases with its aggregation in the fibre^(36,37,38,39,40,41). Weissbein and Coven⁽³⁷⁾ observed aggregates by using the technique of electron microscopy in the case of direct dyes in cellulose, although they could not detect the micelles of low-light fastness dyes, e.g. Sky Blue FF, which dye seems to show aggregation by spectroscopic methods.⁽⁴²⁾

Solov'ev,⁽⁴³⁾ found that molecularly dispersed dyes diffused in gelatin faded most rapidly and the highly colloidal ones most slowly.

In colour photography the dyes formed in the gelatin layer appear to show this same effect: Collins and colleagues in the Research Department of Ilford Ltd. found that when the colour former was used in the developing bath the dyes formed tended to be present in ^{larger} ~~layer~~ particles and to be faster to light than when the former was gelatin-substantive and introduced into the film during manufacture.*

The dye aggregates may perhaps consist of any number from two or

* Footnote: Private communication: R.B. Collins to C.H. Giles, dated Feb. 27, 1962.

three molecules to an unlimited number giving particles which may be visible under the optical microscope. The dye in a state of true molecular dispersion, freely accessible to fading agencies, fades according to the first-order law, with a rate that decreases exponentially with time. Generally in the case of water-soluble dyes an initial rapid fade of first order (or nearly) followed by a slower fade of nearly constant rate is obtained showing that the dye is partly in molecular dispersion and partly in larger particles. Some dyes fade throughout with a constant rate, indicating their presence in the form of large aggregates. Occasionally the rate may increase with time.

The appearance of "negative fading" at first has also been observed in many cases, which means that the intensity of the colour actually increases and it was once believed to be due to phototropic change. ^(44,45) But later on it was proved that it can be due in some cases to the physical breakdown of the dye aggregates, because this effect can be obtained in the dark by heat alone. The "negative fading" can sometimes be reversed by cooling the dyed material in the dark for some hours, when re-aggregation apparently occurs and the depth of colour falls. ⁽⁴¹⁾

Some of the dyes appear from their fading curve to fade according to a second order reaction but little is known of this type of fade.

All fading rate curves ⁽⁴⁶⁾ found in practice can be classified into five main types, shown in Fig. 1. Amongst the large number of fading trials made by the author and previous workers in this laboratory, examples of all five of these classes of curve have been found, as

follows (Table 1).

Lewis and Calvin⁽⁴⁷⁾ suggested that the absorption spectrum of a substance with a planar or almost planar molecule should consist of bands corresponding severally to electronic oscillations along the three perpendicular axes of the molecule. The shorter the axis the shorter the wavelength of its band.

Detection of aggregates by electron microscopy

The high resolving power of the electron microscope along with the improved contrast given by phase-contrast with the optical microscope has made it possible to study the presence of dye aggregates in thin dyed films. In electron microscopy, in order to get a good contrast in the image, the electrons must pass through the specimen without any great loss of energy or scattering. This imposes a limitation on the size and thickness of the specimen that can be used by this instrument. In a newer type of electron microscope, namely the scanning microscope, advantage is taken of the fact that the electron beam used for illumination is not required to pass through the specimen, but is inspected after reflection. Hence objects measuring up to 12 mm. in diameter and several millimeters thick can be inserted in the instrument with little or no prior preparation and can be manipulated in any required orientation whilst under observation.

(49)

According to Gosselett and as found by the author two big difficulties are met while examining textile fibres by electron microscope: frequent destruction of the material examined, because of the

Types of fading rate shown by various
dye-film (or fibre) systems*

- I Acid dyes on gelatin and methyl ethyl cellulose (MEC)
 Merocyanine dyes in collodion
 Basic dyes in gelatin
 Direct dyes in cellulose
 Disperse dyes in hydrophobic substrates
- II Acid dyes in nylon and gelatin (also wool)
 Direct dyes in cellulose
- III Water-insoluble dyes in MEC
 Aggregating acid dye in MEC
 Metal complex direct dyes in cellulose
 Disperse dyes in hydrophobic substrates
- IV Azoic and direct dyes in cellulose
 Mordanted chrome dyes in gelatin
 Mordanted basic dyes in cellulose
 Vat dye in gel (dyed or pigmented)
 Reactive dyes in cellulose
 Direct dyes (fast to light) in cellulose
- V Azoic dyes in cellulose (Cellophane and viscose rayon)

* Footnote

Films are referred to, except as shown.

bombardment by the electron beam and to the consequent production of thermal energy, or to the breaking of chemical bonds as a result of ionization; confused images due to electron absorption when the product is more than 0.2 μ thick.

To make use of the transmission electron microscope to detect minute details, ultra-microtomes capable of cutting slices of tissues of about 100Å. in thickness were developed. Since no methods of obtaining ultrathin sections of dyed fibres for use in high-resolution electron microscopy have been developed, Weissbein⁽⁴⁸⁾ who was the first to detect dye aggregates in dyed substrates, used ultrathin viscose films of about 500-1000Å. thickness.

With electron micrographs of the polyester fibre made by polycondensation of dimethyl terephthalate with ethylene-glycol, the fibrillar structure of synthetic polymer fibres has been established⁽⁴⁹⁾. The setting of the fibrils in nearly cylindrical cords of approximately constant thickness in the whole length was established, and it was shown that the elongation capacity is conferred by the helix fibrils. Irradiation by neutrons produces marked deterioration with attendant reconstruction tendencies of the interfibrillar bands.⁽⁴⁹⁾

Qualitative estimation of aggregation

Lemin and Vickerstaff⁽⁵⁰⁾ following other authors recognised that the absorption spectrum of some dyes consist of two peaks, the one at shorter wavelength due to aggregation (γ -band), and the other at longer wavelength due to monomeric dye (α -band). The aggregation of a dye can

thus be qualitatively estimated by its optical density ratio, i.e. y/x . But this view seems doubtful from results obtained with 1,1¹-diethyl-2,2¹-cyanine bromide⁽⁵¹⁾ which forms large aggregates in the range of concentrations for which spectra have been recorded, but no new band appears (the short-wavelengths band is present even in a very dilute solution in alcohol and is believed to be a fundamental band attributable to the dye structure). Polarographic tests with Methylene Blue⁽⁵²⁾ show that small aggregates are indeed formed, but only at concentrations greater than about $3 \times 10^{-5} M.$, and the size of the aggregates is then independent of the dye concentration even until precipitation occurs. It has been shown by polarographic measurements that the symmetrical 2,2¹-cyanine dye aggregates more readily (as would be expected) than the unsymmetrical 2,4¹-isomer, but the latter dye shows larger metachromatic changes than the first-named one and, on the assumption that metachromatic changes are caused by aggregation of the dye, it would be concluded that the unsymmetrical isomer aggregates more readily⁽⁵¹⁾. Such discrepancies between polarographic results and spectroscopic aggregation hypothesis were also found with Methylene Blue.

The aggregation of dyes in solution has been established^(52,53,54) by many workers.

The following were amongst the conclusions drawn by Giles et al.⁽⁴²⁾

- (a) These x and y bands are present in nearly all dye spectra, both in solution and dyed in transparent films.
- (b) In many cases the change in height of the y-band relative to that of the x-band with increase in concentration is small

(b) (Cont'd)

(ca. 5% for a 100-fold increase in concentration).

(c) The main (α) band of many dyes shifts to longer wavelengths when the dye is adsorbed on cellulose. In the adsorbed state the dye molecules are probably aligned parallel to cellulose chains, and separated therefore by a layer of water molecules.⁽⁵⁵⁾ Krasovitskii and Pereyaslova⁽⁵⁶⁾ found that λ_{\max} for benzidine direct cotton dyes is frequently much higher on regenerated cellulose sheet than in solution, and attributed this to increased conjugation in the dye molecules caused by improved planarity.

Effect of substrates on fading

Generally, the dye has better fastness on more amorphous substrates, if these are hydrophilic. The reason is the presence of larger aggregates of dye which are easier to form in the more amorphous substrates. But this rule is not followed by ^egelatin and wool in the case of acid dyes. It has been found by dyeing rate tests that gelatin has a larger pore size than wool,⁽⁵⁷⁾ yet Kienle et al found that almost every dye has higher fastness (by Fade-O-meter) on wool than on gelatin. Although ~~this data~~ ⁽⁵⁸⁾ give only a rough estimate of the relative dye concentration on both the substrates they show higher concentrations in gelatin than in wool. Hence the higher fastness on wool cannot be due to the concentration difference. Giles⁽¹²⁾ has suggested that the better light fastness of acid dyes on wool might be due to the scattering of the incident light by the rough surface of the wool fibres.

Another hypothesis, which merits examination, is that the higher fastness on wool is due to possible greater absorption of photochemically active (u.v.) light by wool protein than by gelatin, which might be especially important in tests made, as these were, in carbon arc light.

It is usually assumed that the amount of dye which can be adsorbed by polyamides, wool and silk corresponds to the number of cationic sites on the fibre; i.e. the number of amino-groups. If so, the dye would reach a saturation value after which no dye would be adsorbed even if the concentration in the bath of dye is increased.

Zollinger⁽⁵⁹⁾ has demonstrated that the standard affinity, which is the major factor in the energy of dye-fibre interaction is not the cause for the relatively high light fastness of basic dyes on polyacrylonitrile fibres. The following mechanism has been suggested by him for the low light fastness on fibre substrates containing carboxyl groups, but without sulphonic groups, i.e. cotton or wool.

By irradiation, the ion-pair consisting of a dye cation and a carboxylate anion of the substrate forms an excited state, in which an electron is transferred from the anion to the cation. The resulting carboxyl radical loses, in an irreversible step, carbon dioxide, a recombination of the radical cation becomes impossible and the dye radical decomposes irreversibly (probably by a primary reductive step). With sulphonate groups present, however, as in commercial acrylic fibres this type of reaction is much less probable, as sulphonate anions have little tendency to form radicals and thus to lose SO_3 . The excited state

regenerates therefore the ground state and the rate of light fading is slow. This rate follows the Hammett relationship because substituents with positive σ -values increase the stability of the ion-pairs or because they facilitate the redistribution of charges in the reverse stages of the formation of the excited states.

Zollinger's results agree precisely with the oxidation hypothesis of Gunning et al. but at the same time Zollinger has rather inexplicitly claimed that for this very reason one should not agree that this hypothesis is correct. He gives some other alternative explanations, most of which seem to be more complex than that of Gunning et al., except possibly that which suggests that Hammett positive sigma-value substituents improve fastness by favouring aggregation. Nevertheless this would not explain why these groups act in an opposite sense in dyes on protein substrates.

On one point he is not consistent with his explanation. He says the Hammett relation did not hold for fading on tanned cotton, but it should do so, on his ion-pair hypothesis, if the tannin mordant acts as a source of carboxyl ions.

Gunning et al. showed that the Hammett effect was reversed on proteins, but according to Zollinger's ion-pair hypothesis it should not be so. Thus all the facts so far known support best the oxidation process hypothesis.

Light fastness of dyes on polyacrylonitrile fibres is stated to be higher than on other fibres, and some attempts by Zollinger and Wegmann

have been made to explain this in chemical terms. But some of the facts given by other workers should be examined first, before discussing these suggestions.

There are two types of dyes, namely disperse and cationic (or basic) which are mostly used for dyeing this fibre, and according to the data quoted by Giles, disperse dyes are up to $1\frac{1}{2}$ grades faster on Orlon (a polyacrylonitrile fibre) than on (dull) secondary cellulose acetate,* the cationic dyes are up to 3 grades faster on Orlon than on tannin - mordanted cotton and most (not all) are faster on Orlon than on Wool (up to $2\frac{1}{2}$ grades, though some dyes are less fast on Orlon than on Wool).

The higher crystallinity of Orlon compared with other fibres, which may restrict the diffusion of moisture to the fading sites of the dye inside the fibre, is perhaps responsible for the better light fastness of dyes on this fibre. Nevertheless Wegmann has suggested dye-fibre covalent bond formation as the main factor responsible for higher light fastness on Orlon in case of basic dyes. This hypothesis was discussed by Giles and Mackay⁽¹²⁾ who quoted results obtained by Dragebū which cast doubts on its validity; e.g. the reversal of relative fading thus expected on transference of a pair of dyes from an anionic to a cationic fibre was not observed.

* Footnote: The dulling agent (TiO_2) has a slight effect in reducing, light fastness, but not enough to invalidate these comparisons. (2,35,60)

Effect of temperature and moisture on fading

The temperature coefficient of fading is low and change of temperature has an indirect effect on the rate of fading, by influencing the moisture content of the fibre. An increase in moisture content can cause a very large increase in fading rate of some dyes, on cellulose in particular. There is lesser change in case of wool. (61)

Most dyes show better light fastness with higher fibre regain, but in many cases where the fibre has a very low fibre regain (e.g. polyesters) the reverse is true. (2,35,60) It has been suggested that this anomalous behaviour of dye on polyester fibre is due to two causes: firstly, the absence of sufficient moisture in the substrate to sustain the fading reaction under test conditions, and secondly, to the dye being trapped between the molecular chains of the hydrophobic substrate, where moisture cannot reach.

Hedges⁽⁶¹⁾ found that a rise in humidity accelerated fading in all cases and that a linear relation exists between percentage loss of dye and the moisture content of the sample, at least down to about 5% moisture content, for a number of dyes on cotton or wool. The formula proposed by him is $F = K \sqrt{T} (R + C)$, as a means of predicting fading under different conditions. (F = % loss of dye, K , C are constants, T is temperature, and R the regain of the fibre).

The moisture regain actually required for the fading reaction is very small. The fact that the above effects are observed at relatively high regains indicates that the fibre pores are perhaps blocked by dye.

This blockage of fibrespores differs from dye to dye; every dye has a different blocking effect on different fibres and different dyes have different effects on one fibre. This blockage in turn restricts the flow of water vapour molecules to the fading sites. Elder and Tolia⁽⁶²⁾ found evidence of such blockage during measurements of the adsorption of vapours of aliphatic alcohols or water by dry wool. Larose⁽⁶³⁾ found that the water vapour adsorption of wool is reduced when a dye (Orange II) is present, though he attributed this to a purely chemical effect.

Introduction to the present work

It has already been pointed out⁽¹²⁾ that the light fastness of dyed materials depends on a large number of different, unrelated factors and the mechanism is complex and little understood. The author wished to investigate the effects of several of the possible factors with a view to building up a background of experimental facts on which a comprehensive theory of fading should rest. Factors studied include the formation of dye-fibre bonds, the effect of humidity on fading on polyester or polyacrylonitrile* films of different orientation; the ~~decreased~~ improved light-fastness of acid dyes on gelatin compared with wool; the fading rates of dyes used in previous electron-micrographic studies of fading; the y/x -band ratio of various dyes in various media; the fading rates of film in glass slides and in metallic slides. All of these factors have a direct bearing on the actual light fastness of dyed materials.

* Results not yet ready

Effect of dye-fibre bond strength on
the light fastness of reactive dyes.

With reactive dyes the dyeings do not depend upon the physical adsorption and mechanical retention to give an excellent wet fastness property. But how far the light fastness is affected by this dye - fibre bond is yet to be ascertained. During the last fifty years many workers have suggested that dye-fibre bonds affect the light fastness of dye, by passing on absorbed light energy to the substrate and thus diminishing the likelihood of the primary photolytic breakdown of the dye. Thus Gebhard^(6,7) stated that light-fastness rises with the strength of the dye-fibre bond. A relation between light fastness and wet fastness in a variety of dye-fibre systems was found by Schaffer⁽⁶⁴⁾. Wegmann^(65,66) showed an increase in light-fastness of basic dyes on polyacrylonitrile, with the formation of a covalent bond rather than an ionic bond, with the fibre. Gill⁽⁶⁷⁾ suggested the cause of the susceptibility of direct dyes (on cellulosic fibres) to photo degradation, when in presence of cationic agents, to be weakening of van der Waals forces between the cellulose chains and the dye molecules, which thus cannot pass light energy to the cellulose so readily in the form of heat.

Similar reasons have been given for an improvement of the light fastness of the reactive dyes on fixation to the fibre which is discussed later on.

Chemistry of the reactive dyes

The general formula for a reactive dye is⁽⁶⁸⁾



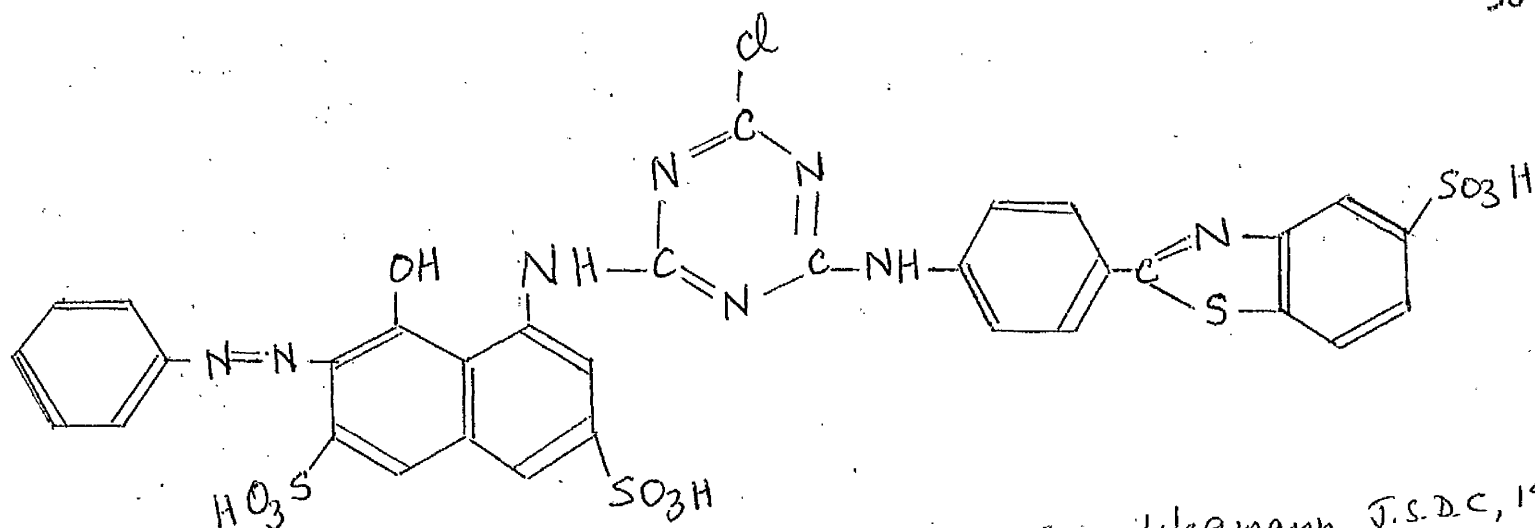
where, S = solubilising group; D = coloured portion or dye which may be an anthraquinone or an azo dye, etc; G = portion of dye molecule holding the reactive element; and X = the reactive group, which reacts with the cellulose molecule.

The reactive dyes are generally made deliberately with low affinity for cellulose without loss of fixation and colouring power. The reason for this⁽⁶⁹⁾ is that the dyes of low molecular weight and simple structures can then be attached to cellulose in a way that gives high wet fastness and produces bright colours. The complex structures of higher affinity would tend to give dull shades. The low molecular weight and high solubility of the dyestuffs give outstanding levelling and diffusion properties before reaction occurs and make cold dyeing possible ^{with} ~~on~~ these reactive types requiring low temperatures. Moreover this makes it easier to remove the hydrolysed dye from the fibre after the dyeing operation is finished.

The reactive dyes are generally based on the following structures :-

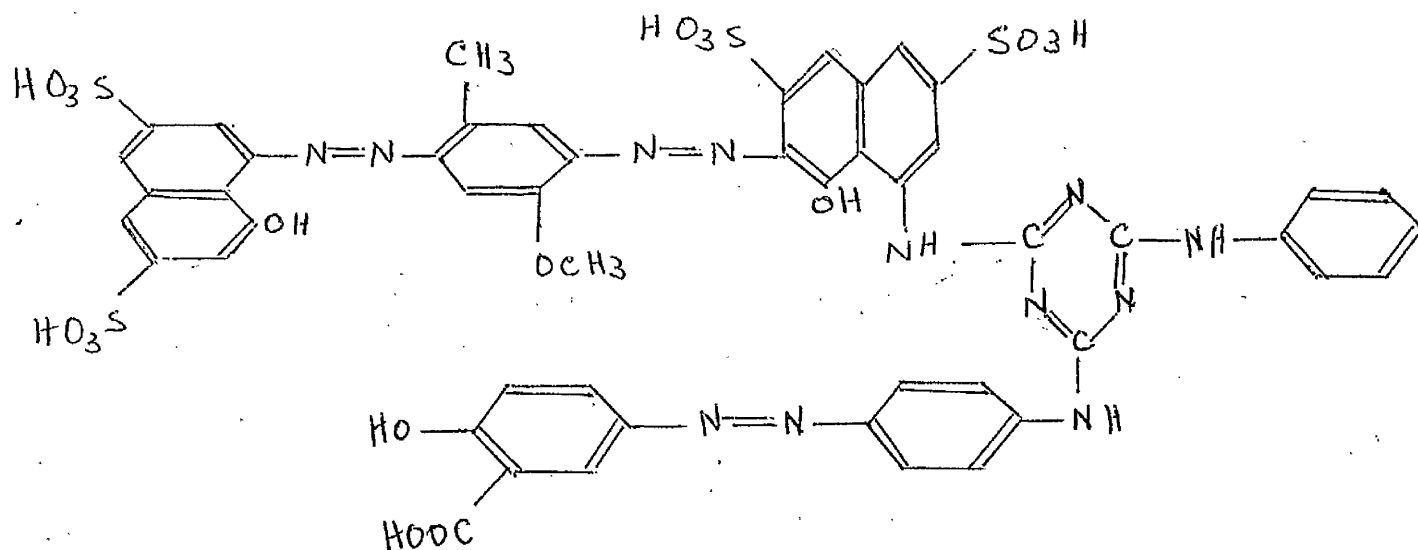
(a) Cyanuric Chloride residues

The reaction of dyestuffs based upon the monochlorotriazine group, with cellulose, to form a stable chemical linkage (covalent bond) was accomplished as early as 1930 by Haller and Heckendorn^(70,71). Examples are



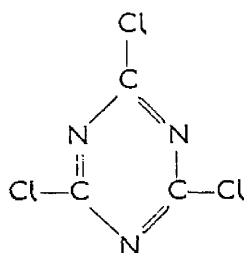
see Wegmann, J.S.D.C., 1965
76 205

G.I. Direct Red 71

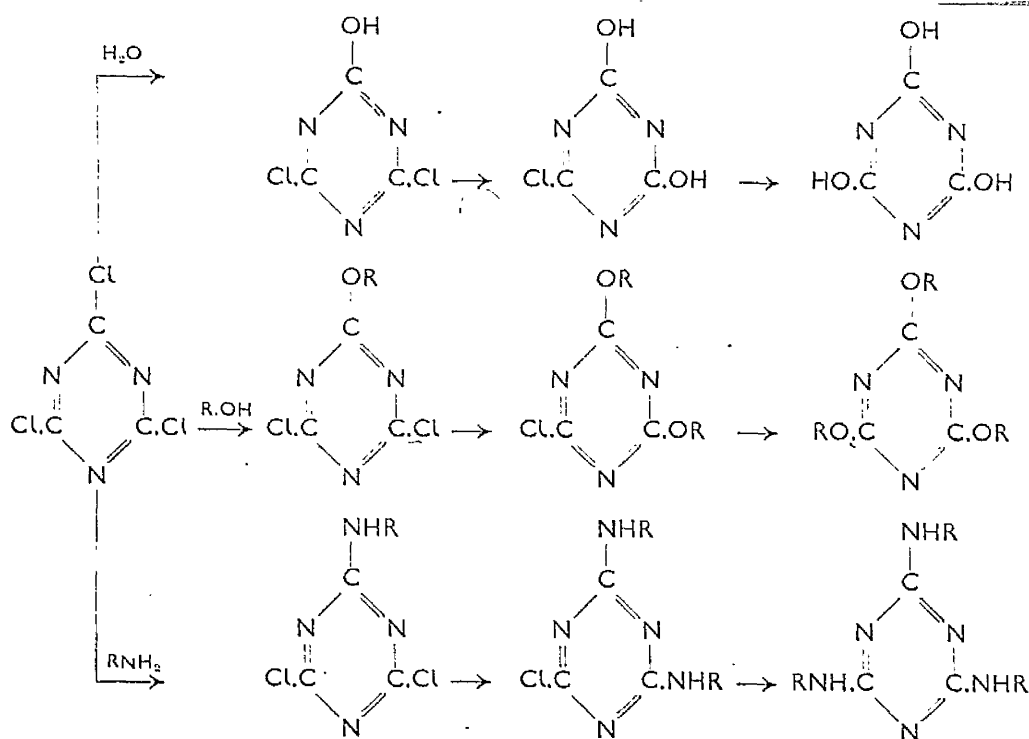


G.I. Direct Green 26

Procion and Cibacron dyes are of this type. The three labile chlorine atoms in cyanuric chloride can be made to combine with one, two, or



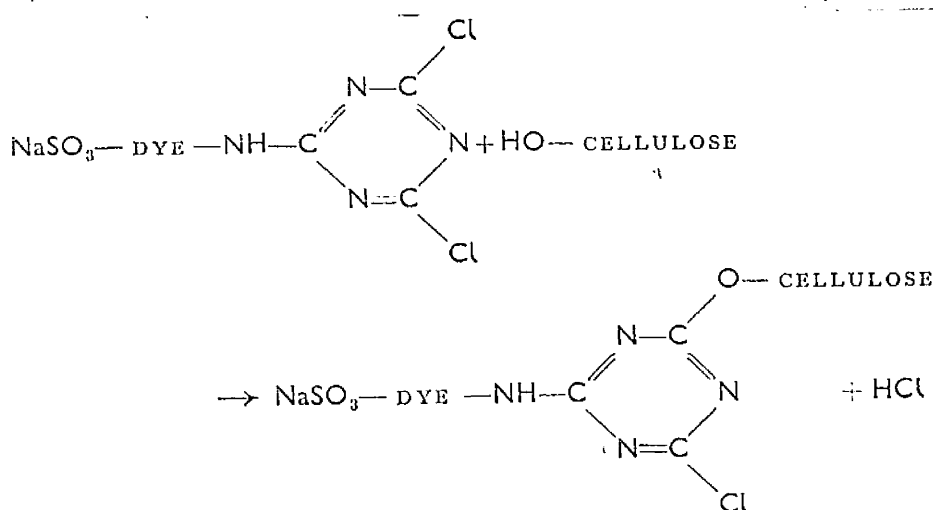
three compounds containing hydroxyl or amino groups, under an alkaline condition. The substitution of only one chlorine of the cyanuric chloride ring with a dye molecule gives a dichloro-s-triazinyl dye, which is considerably more reactive than dyestuffs in which two chlorine atoms of the triazine ring have been substituted. These dyes react with water, alcohols, and amines⁽⁷²⁾ as shown below.



The unsubstituted one or two chlorine atoms of the cyanuric chloride will react with the hydroxyl groups of the cellulose^(73,74,75) at 20°C (68°F). There are two types of Procion (ICI) dyes which are based on this reaction:

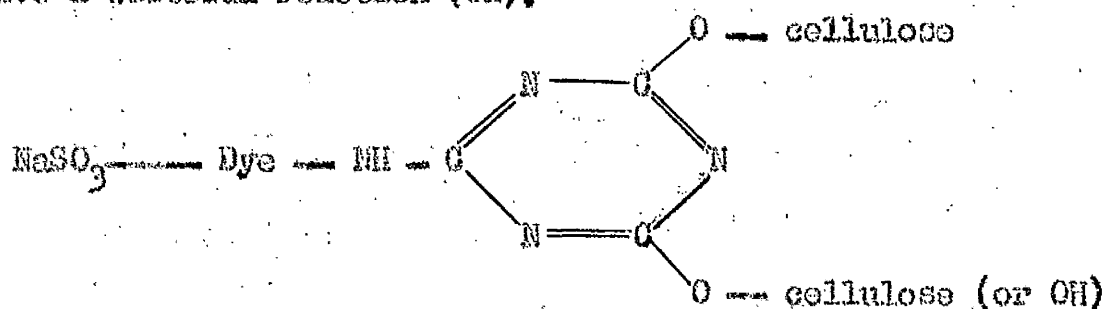
- (a) Procion cold-dyeing dyes having two active chlorine atoms which react at 20°C (or cold) (dichloro-s-triazinyl dyes)
- (b) Procion hot-dyeing dyes having one active chlorine atom which reacts at 60°C (or above) (monochloro-s-triazinyl dyes)

Reaction with cellulose

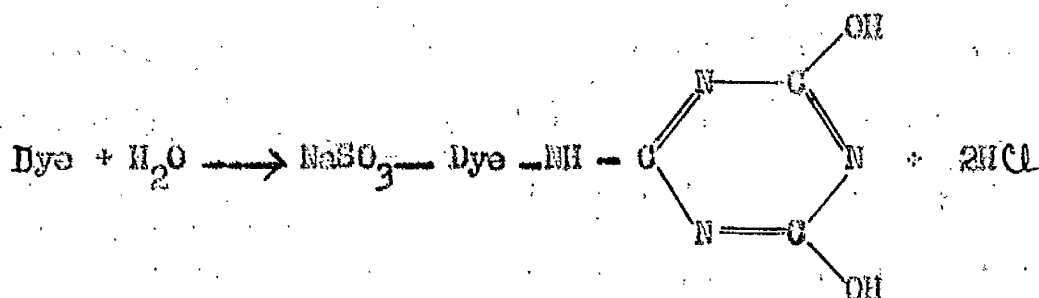


The above reaction takes place in the case of the dyes having one active chlorine atom but in case of dyes having two active chlorine atoms the reaction can go a stage further at higher temperatures, and greater alkalinity than normal, shown by significant reduction in swelling in cup/rammonium hydroxide solution or may react with dyebath

to give a wasteful reaction (OH).



Such dyes however have a great tendency to undergo hydrolysis with water.

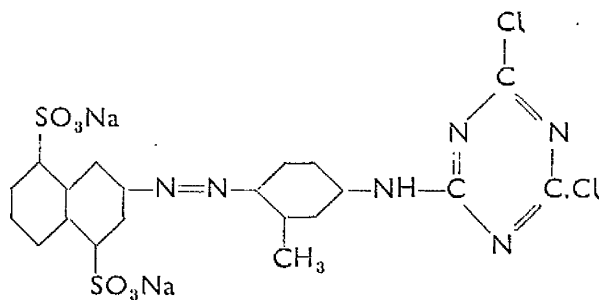


This hydrolysed product decreases the colour yield and reduces the wet fastness of the dye as it does not form covalent bonds.

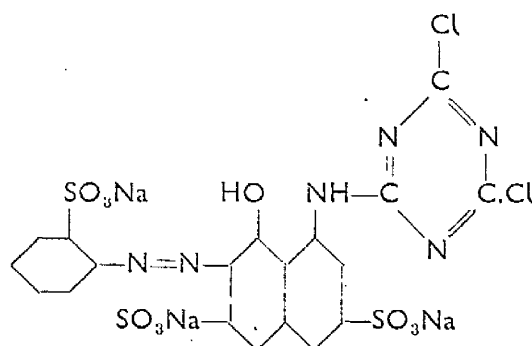
Sometimes an acetal and not the ether linkage is formed. These acetals are unstable, particularly under acid conditions, although they are also covalently fixed to the fibre⁽⁵⁹⁾.

With the dichloro-s-triazinyl dyes a reaction is possible between the primary or secondary hydroxy-groups of the cellulose chain in seven possible combinations⁽⁷⁶⁾. With monochloro-s-triazinyl dyes only two combinations with these cellulose groups can occur, i.e. with either primary or secondary groups. The rate of reaction with secondary hydroxy-groups (if at all) is very slow and would form a minimum of bonds.

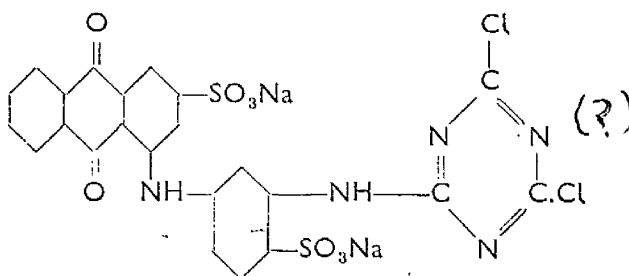
Typical structures of Procion type dyes are: (77)



(77)
Procion Yellow



(57)
Procion Red



Their substantivity for cellulose increases with the presence of an electrolyte. In neutral solution physical adsorption takes place, but the formation of covalent bonds takes place only in the alkaline medium. (65,78)

Evidence for a chemical reaction with the fibre

- (1) The colour can be washed out with water before adding alkali, but afterwards it is fast to boiling soap solution.
- (2) Other dyes, e.g. direct, azoic and vat dyes, can be stripped by pyridine on boiling but the reactive dyes cannot, after their fixation, suggesting that some force other than adsorption or mechanical retention is holding the dye to the fibre.
- (3) Polyvinyl alcohol is regarded as similar to cellulose in its chemical activity and when its aqueous solution containing on the one hand Procion dye, and on the other, an acid or a direct (unreactive) dye, are poured on the surface of a solution of caustic soda saturated with salt, they react differently. When the Procion dye is present a film is formed which can be boiled with water without disintegrating, but a film formed with direct dye under similar circumstances disintegrates rapidly and dissolves.
- (4) Cellulose fibres dyed with Procion dyes do not dissolve in cuprammonium hydroxide solution as distinct from fibres dyed with direct dyes. This fact and the behaviour of the polyvinyl alcohol film suggest very strongly that reaction with the hydroxyl groups of the polymer has occurred to change its solubility. But Nevell's⁽⁷⁹⁾ work shows that some cold-dyeing Procion dyes do not make cellulose insoluble in cuprammonium hydroxide, whereas some hot-dyeing Procion dyes do. This

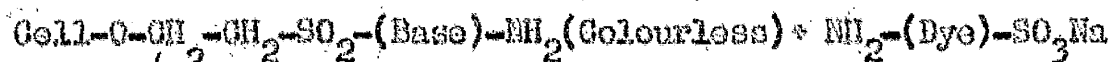
(4) (Cont'd)

clearly indicates, therefore that cross-linking of cellulose cannot alone account for this behaviour. Schwertassek⁽⁸⁰⁾ reported that the bifunctional reactive dyes (i.e. dichloro-s-triazine dyes) though capable of cross-linking, show a one-ended reaction with the hydroxy-group of cellulose, resembling monofunctional dyes. This anomalous behaviour in cuprammonium solution is suggested to be due to the fact that dyed cellulose absorbs more copper ion as the dye concentration increases. Formation of Cu-dye complexes has been observed with hydrolysed purified Procion dye in neutral and ammoniacal solutions, by means of Job's method. Mehta et al⁽⁸¹⁾ have suggested the formation of copper-dye complexes as the cause of the abnormal viscosity of Procion dyed cellulose and not the dye-fibre bondage.

- (5) The presence of an azo group may be used to obtain the colour of a reactive dye. Consequently this dye can be reduced on the fibre by sodium hydrosulphite to ^{two} α -amino-containing products. If the dye has reacted with the fibre before reduction, one of these products should remain anchored to the fibre and should resist washing out. Such a "discharged" fibre can in fact be diazotised and coupled with another phenol or amine to produce a new unreactive or direct dye, and this process can be repeated indefinitely.

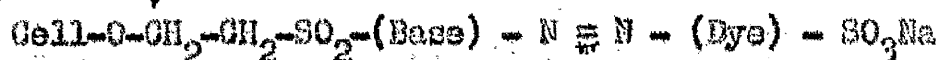
(5) (Cont'd)

(a) Cell - O - CH₂ - CH₂ - SO₂ - (Base) - N = N - (Dye) - SO₃H reduce →

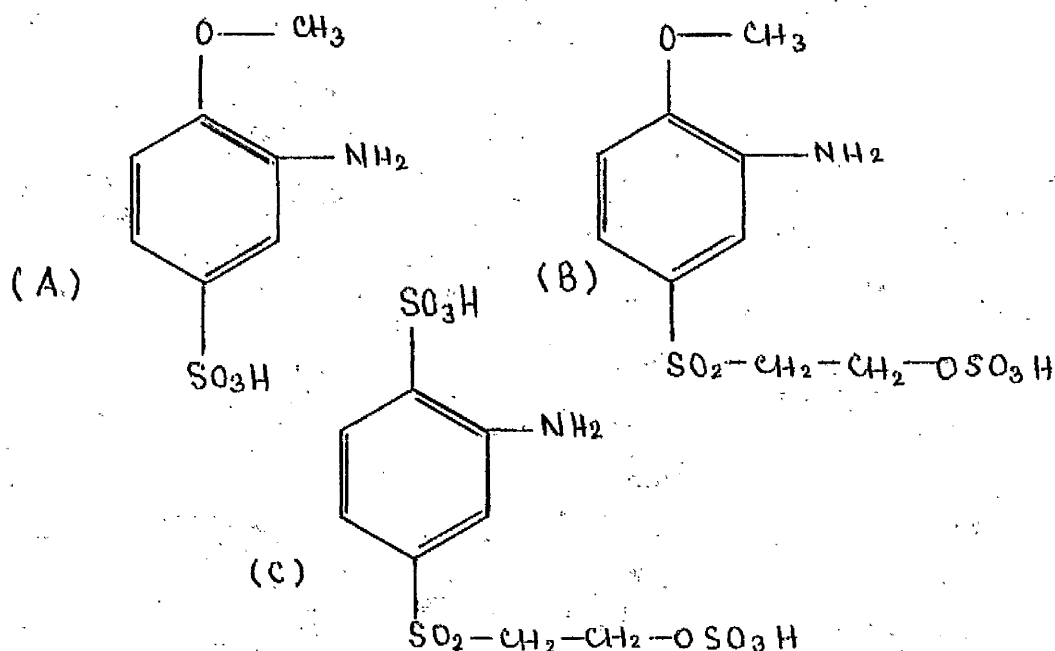


diazotised

(b) Cell-O-CH₂-CH₂-SO₂-(Base) - N⁺≡N⁺Cl⁻ + NH₂-(Dye) - SO₃Na



(6) A base containing a reactive group can be applied ^{followed} by diazotisation and development on the fibre to give a coloured body. The three bases listed below can be applied to cellulose and then washed. But on diazotisation and coupling



with 1-naphthol-5-sulphonic acid, only B and C gave fibres which were coloured.

- (7) If cellulose is dyed with reactive dye and then acetylated, and the acetic acid solution then poured into water, the dyed cellulose acetate is precipitated with very little dye going into the aqueous phase. If the same experiment is repeated using direct dye, most of the dye leaves the precipitated cellulose acetate and bleeds into the aqueous dyebath.

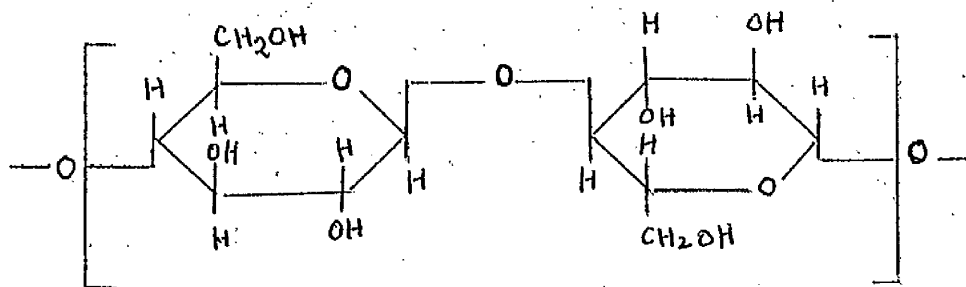
But concurrently with the fixation of the dye to the fibre the dye also becomes hydrolysed^(66,76) in alkaline medium giving mono or dihydroxy compounds. These are easily washed out on boiling with soap solution. But once the dye is fixed it cannot be hydrolysed, if the alkalinity of the fibre is neutralised. The most important fact is that the rate of reaction of the dye is much faster with most organic compounds than with water, e.g. α -methylglucoside reacts seven times as fast as with water. Hence excessive hydrolysis will not take place before the dye has had time to combine with cellulose.

Evidence for the site of reaction in cellulose

Cellulose contains both primary and secondary alcohol groups but it is believed that the reaction takes place preferentially with the primary alcoholic side chains.⁽⁷⁶⁾

It is thought that^(78,82,83) the site of attachment is at the primary hydroxy group located at the C6 atom of the glucosidic unit of cellulose. Other evidence indicates that the secondary hydroxy-groups do react with

some of the reactive dyes (76,84)



Accepted conformation of the cellulose molecule

Both primary and secondary hydroxyl-groups will differ in their reactivity towards cellulose reagents e.g. the secondary group at C_2 is more acidic, and under basic conditions necessary to achieve reaction, this group could conceivably react with the reactive dyestuffs. The primary group at C_6 is thought to be the most reactive, due to the fact that it is really a hemiacetal. These groups are present in the end-groups of the polymer chains and may be readily available for possible reaction with the dyestuffs. It is quite possible for reactions used to synthesise cellulose derivatives (such as reactive dyeings) to involve the secondary as well as the primary hydroxy-groups. The terminal group at C_4 is quite unreactive and probably does not take part in the formation of a dyestuff-fibre bond. These groups would only be available in the end-groups of the polymer chains.

Some dyes do not react with sodium alginate, which differs mainly from cellulose in the fact that it contains carboxyl groups, instead of the primary alcohol groups located at C_6 in cellulose. This indicates that the primary hydroxy-groups of cellulose are the ones involved in

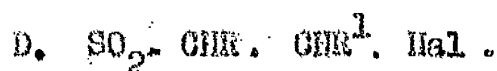
the reactive dye-cellulose reaction. Yet, dichlorotriazine dyes have been shown to react with calcium alginate, indicating that these dyes are capable of undergoing reaction with the secondary hydroxy groups located at C₂ and C₃. These dyes also react with sodium alginate under basic conditions.

If a cuprammonium solution of cellulose is treated with a reactive dyo, and if, after the reaction has been completed, the cellulose is regenerated by the addition of acid, a fast-dyed cellulose is obtained. It has been proved that the secondary hydroxy-group of cellulose is blocked in cuprammonium solution, therefore it cannot enter into the cellulose-dye linkage⁽⁸⁵⁾; yet, if it were not blocked, reaction at this group may have occurred.

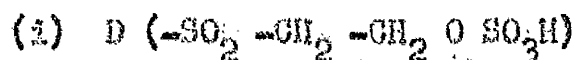
Srivastaya et al⁽⁸⁶⁾ have further suggested the view that most of the reactive dyes react predominantly with primary hydroxy groups, although very reactive types also react with the secondary alcoholic groups. Some dyes (e.g. Remazol Red B and Procion Brilliant Red H3B) react exclusively at primary hydroxy groups. Thus cellulose which has been modified so as to increase the number of primary hydroxy groups in the accessible region, upon dyeing with reactive dyes shows increased rate and extent of dye uptake.

(b) Based on vinyl sulphone

Remazol and Remalan dyes⁽⁸²⁾ are the examples of this class. These originated from the idea of dyes of the general formula -

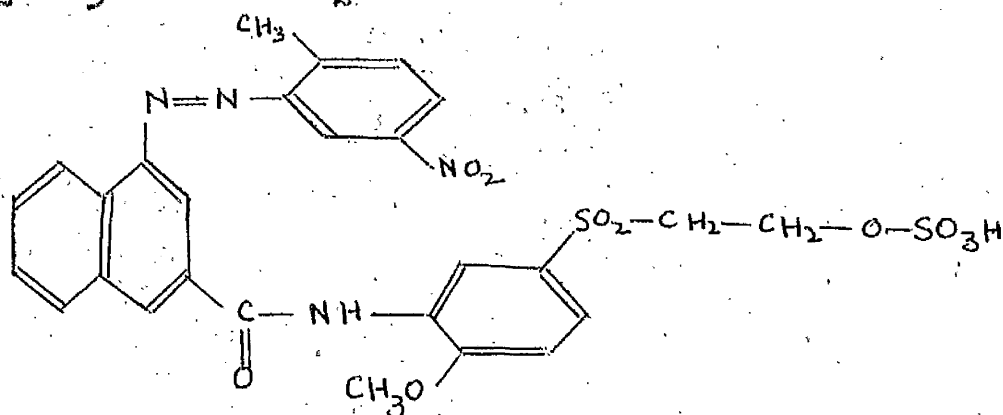


In general R and R¹ = H, low-molecular^{wt}/alkyl, or halogen, the simplest cases of this are



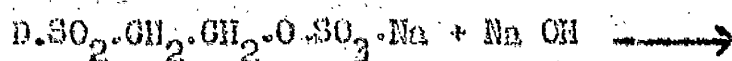
D, the dye molecule contains one or more solubilising groups.

The above mentioned same general formula S - D - G - X; where X = -CH₂ -CH₂ -SO₃H and G = SO₂ can be applied here as well.

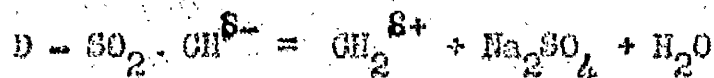


A typical dyestuff of this class.

In alkaline medium the following reaction takes place.

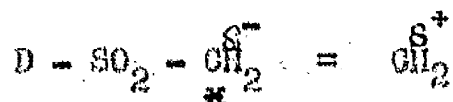


unreactive and stable dye



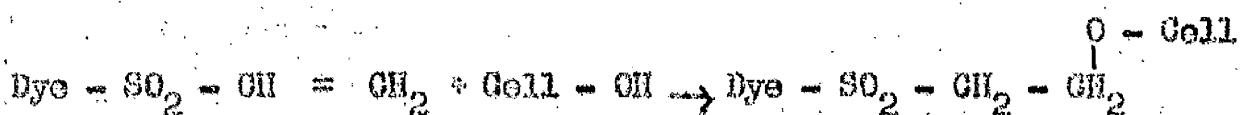
reactive dye element

These dyes do not change in neutral aqueous solutions, thus they are resistant to hydrolysis. The vinyl sulphone group^u, as a result of the mobility of the π -electrons in the double bond show very strong polarisation effects due to the presence of the -SO₂-groups :-



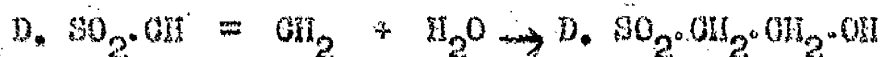
The carbon marked * has an electron attraction effect thereby inducing negative character, while the carbon atom in the β - position becomes positive in nature.

These dyes can undergo additional reactions with hydroxy groups in water, alcohols and cellulose :-



The hydrolysis of these dyes during dyeing is favoured by increase in temperature and pH :-

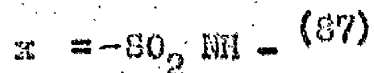
(the product given is hydroxyethyl sulphone)



(hydroxyethyl sulphone)

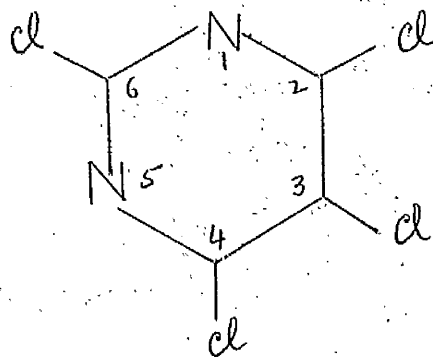
Here the dye-fibre linkage (ether linkage) can be split by the action of alkalies at higher temperature. The other dyes of this class (i.e. vinyl derivatives) are -

Primazin dyes, where $x = -NHCO -$ and Levafix dyes, where

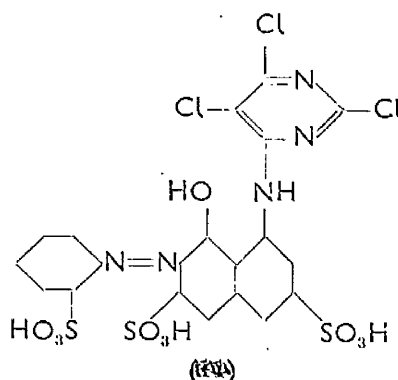


(c) Based on tetrachloropyrimidine

Reactone and Drimarene dyes are the typical examples of this class.



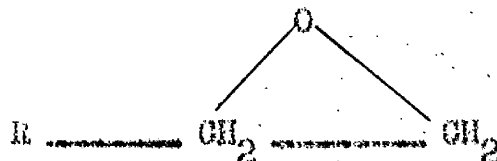
Unlike the Procion dyes here all the chlorine atoms are not equivalent. These dyes have an excellent stability to alkali. Condensation reactions occur first at C₄⁽⁸⁸⁾ and then at C₂ and lastly at C₆, but with cellulose fibre the dyes react at C₂⁽⁸⁹⁾. The chlorine atom at C₃ is unreactive



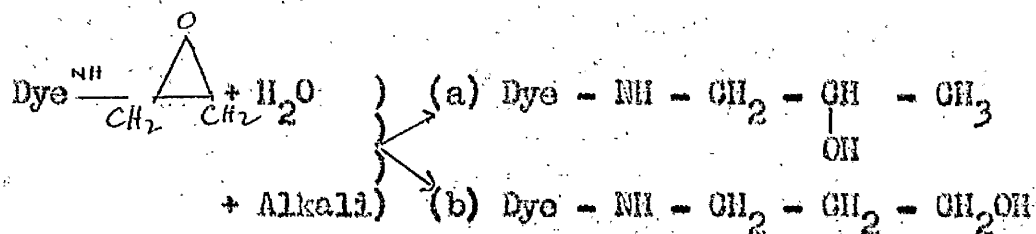
Reactone Red 2B

(d) Based on an epoxy group

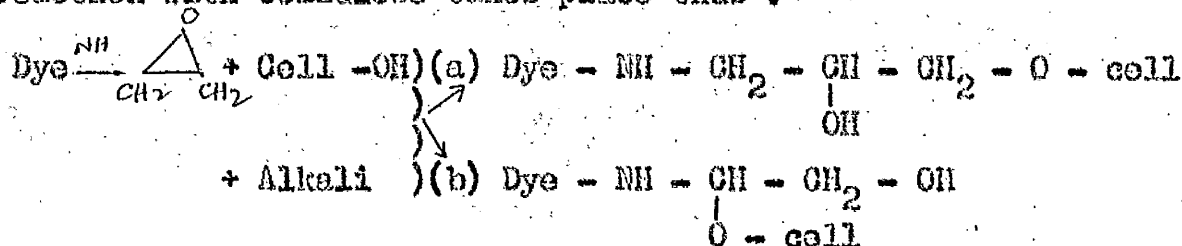
Epoxydes have been used for some time to form permanent bonds with the cellulose polymer, especially in resin finishes. It is possible to form either a primary



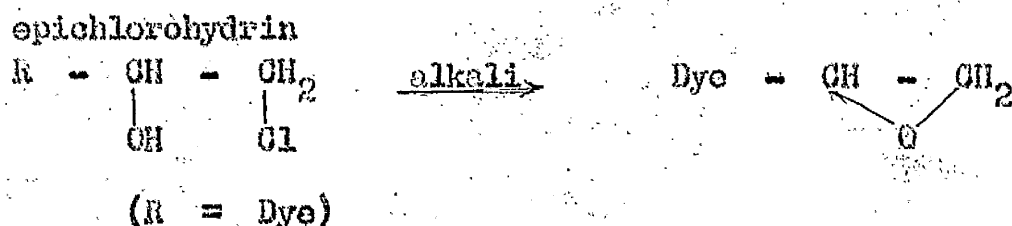
or secondary ether linkage with hydroxy-containing polymers, depending upon which way the epoxide ring opens. The reaction with water can occur to give the wasteful reaction.⁽⁹⁰⁾



The reaction with cellulose takes place thus :-



Here, either a primary or secondary ether linkage with cellulose is formed depending upon which way the epoxide ring opens.



If epichlorohydrin is used to form the reactive centre the epoxide could be obtained in situ by treatment with alkali. The dye thus produced with phthalocyanine dyes linked through an amino-bridge possesses an excellent stability to heat, light and chemical reagents and such dyes may contain suitable solubilising groups, e.g. sulphonic or carboxylic acid groups, for ease of application.

Previous work

To test the importance of dye-fibre linkage in the case of reactive dyes Ingamells⁽⁹¹⁾ made some experiments which were based on the fact that when crease-resist resins are used on dyed fabrics, very often the light-fastness of the dye deteriorates. The application of resin

precondensate alone, without the hot acidic conditions (curing) necessary for the postulated condensation reactions, is sufficient to cause deterioration in fastness to light, and a simple washing-off treatment applied to the uncured fabric will restore the original fastness⁽⁹¹⁾. This behaviour would obviously be impossible if the formation of covalent linkages was responsible for the observed effects on light fastness.

Ingamells suggested that during illumination crease-resist resins become a source of reactive oxygen for the photolytically excited dye. He compared the effect of resin on the light fastness of the reactive dyes on cellophane film. One set of cellulose fibres was "ring" dyed i.e. the fibres were not fully penetrated and the other was fully penetrated. He found that there was more rapid fading in the case of fully penetrated dyeings. This might seem to support the observations of Baxter et al^(36,39) that a change in the dye in the fibre from a dispersed state to an aggregated or crystallised state is accompanied by an increase in light fastness, because a smaller area per unit weight of dye is exposed to agencies involved in photochemical attack.

But in practice, the dyeings are in between these two extremes, i.e. neither fully ringdyed nor fully penetrated, depending upon the affinity of dye and the method of application. Hence it is quite possible that the affinity of the dye for the fibre may show its effect in its susceptibility to photochemical attack by this indirect means.

With this idea in mind Ingamells made two sets of dyeings of dichlorotriazinyl reactive dyes on cotton -

(a) monohydroxy-monocellulose linkage (fixed dye) and

(b) unfixed, purified dihydroxy-dye.

He found that the fixed dyeings were faster than the unfixed. The reason he gave was that the fixed dyeings were well dispersed in the fibre, otherwise they would have faded rapidly. According to Shaeffer's⁽⁹²⁾ views, this better fastness is due to the covalent linkage which facilitates the transfer of photochemical energy from the dye to the fibre, thus resistance of the dye to the photochemical attack is increased.

Osawa et al⁽⁹³⁾ found that the whiteness of fluorescent polymers on a non-fluorescent material is faster to washing and abrasion than that obtained from an ordinary fluorescent brightening agent. They obtained one set of copolymers of acrylonitrile and methyl acrylate with which the fluorescent brightening agent was also copolymerised. In the other set of copolymer of acrylonitrile and methyl acrylate the fluorescent brightening agent was finely dispersed; the ratio of brightening agent to monomer mixture being approximately the same in both the cases.

On irradiation to a Xenon lamp, it was noticed that the polymer containing the brightening agent as a part of the side chain faded more slowly than that in which it was attached to the surface of the polymeric particles⁽⁹³⁾. If the degree of aggregation of fluorescent groups would have been responsible for the rate of photodecomposition, then the copolymer having finely dispersed brightening agent would have shown better light fastness than the one having it as a part of the side

that it did not
 chain, was explained by them as being due to the transference of part of the absorbed energy from the brightening agent to the polymer chain by the covalent linkage between the molecules of the agent and the copolymer of acrylonitrile-methylacrylate. They further suggested the same reason for the decrease in the rate of photodecomposition of reactive dyes on cellulose.

Chokalin⁽⁹⁴⁾ confirmed that the reactive dyes become a part of the fibre, covalently linked. The union between glucose units and the dye is stronger than that between the glucose residues themselves which builds them into cellulose. Stamm and Zöllinger⁽⁹⁵⁾ showed that cellulose coloured with reactive dyes of the Remazol type could be broken down to ethers of cellobiose and glucose without breaking the bonds between the dyestuffs and the glucose residues.

Reactive dyes although having covalent ~~union~~ bonding with the fibre, show aggregation in the solid substrate⁽¹²⁾. Their intermolecular forces are therefore sufficiently powerful to cause aggregation even when one point of the dye molecule is covalently linked to the fibre molecular chain. During the reaction with the fibre the system is, of course, in an aqueous medium, and the fibre molecules accessible to dye will be solvated by water and flexible enough to accommodate themselves to the positions taken up by the aggregated dye molecules.

If however the dye-fibre bond strength is entirely responsible for the light fastness of a dye then fastness should be the highest in the case of monodisperse dyes as the dye-fibre bonds are reduced in strength with increase in depth of the shade. (This is because the most active

sites are filled first). Then the reactive dyes would be fastest to light of all dyes as they have the strongest dye-fibre bonds (the covalent bonds), but they are not so. Also it has been shown by the author that the reactive dyes have better light fastness on gel-Gellophane than on normal Gellophane and it is well known that they are faster on viscose than on cotton⁽³⁵⁾. With direct cotton dyes even varieties of viscose rayon and regenerated cellulose films differing only in crystallinity show these effects⁽³⁶⁾. But the chemical structures of these substrates are the same, so the number of dye-fibre bonds will be the same in every case.⁽⁷³⁾ Hence it might appear that the only factor which could be responsible for this higher light fastness of the reactive dyes after fixation is aggregation, which could be greater in the case of more amorphous substrates such as gel-Gellophane and viscose rayon than on the less amorphous cotton and normal Gellophane.

Durand and Huguenin A.G. (Basle), showed (private communication) that the light fastness of some acid dyes on films decreased when covalent bonding occurred. They took five dyes of different classes having $-SO_3H$ and $-PO_3H_2$ groups and dyed alumina and wool in two different depths of each dye. All the dyes having an $-SO_3H$ group could be desorbed from the alumina film (unsealed) in hard water but the dyes having a $-PO_3H_2$ group could not be desorbed. Therefore, it was concluded that the dyes having a $-PO_3H_2$ group are covalently bonded with alumina. When the effect of light was examined on the films and on wool, both dyed with the same dyes, it was noticed that the light fastness decreased in

the case of alumina, while it remained the same on wool. This shows that the covalent bonding decreases the light fastness of a dye, which is quite contrary to the hypotheses based on observations discussed above.

The higher ratio of γ/α -band spectral absorption on gel-Cellophane compared with normal Cellophane, in the case of reactive dyes, as described below, further supports the suggestion that aggregation is an important factor in the better light fastness of reactive dyes after fixation on cellulose.

Effect on direct dyed Cellophane fading rates of
alternating irradiation and storage in the dark

It has been shown that fading is very slightly greater in cold atmosphere than in hot, probably because the substrate then contains more moisture. The initial rise in optical density sometimes noticed is probably due to the breakdown of the dye aggregates caused by heat (as it has been reproduced by heating the dyed films in the dark). The density rises linearly with temperature up to a limiting temperature.

It was noticed further, that, when a dyed Cellophane film was subjected to alternating irradiation and storage in the dark at 55°C., the optical density falls on cooling in the dark, but rises again when the lamp is switched on. (Both the changes are much greater at high humidity than at low humidity). This type of continuing fade in the dark, observed with various types of dye has been attributed by earlier authors to a continuing chemical action caused by peroxide, produced photochemically during the irradiation, but the reversibility of the change shows this explanation

untenable in this particular case. This experiment was first made by S.M.K. Rahman here, and was repeated by the author in the course of preliminary checking tests.

Difference in fading of direct dyes in glass slides and in open exposure

During earlier work in the laboratory it was noticed that fading is more rapid in open exposure of films to light than when they are bound in between two glass slides (Fig. 3) It was therefore considered necessary to examine the cause of this effect before the main investigations were started, since most of the projected work would involve fading of mounted films.

Effect of external roughness of the film on dye fading

Gelatin being more amorphous than wool, should include larger dye aggregates leading to better light fastness of dyes than on wool, but in fact the reverse occurs. A possible cause for this is the scattering of incident light by the scales present on the wool fibre, so that the light actually reaching the dye is weakened.

The results of Weissbein and Coven's tests correlated with fading rate curves

These authors, who used direct-dyed cellulose film, were the first to reveal the aggregation of dyes in any substrate by electron microscopy. The same dyes were tested by fading rate to find whether results agree with electron microscopy.

The y/x-band ratio of different dyes
in different media

The ratio of y/x bands of a dye in any medium is believed to give, in many cases, a qualitative measure of its aggregation. Hence this work was undertaken to correlate the relative degree of aggregation in certain substrates with the light fastness of dyes therein.

Effect of dye layer thickness on fading

In theory, monodisperse dye, evenly illuminated, would show first-order fading. If the light intensity is reduced, the rate constant is also reduced but not the order of fading. In a film or fibre exposed to a source of light, the dye at different depths is exposed to different intensities of light - maximum at the surface nearest to the light source, minimum at the opposite surface - because of the absorption of light by the successive layers of dye the light traverses. However, the total fading would be of the first order and the rate constant would be an average of those for each successive layer. In a very heavily dyed material the light which causes fading might be almost completely absorbed (e.g. an optical density of 2.0, which would be shown by a heavily dyed film, represents 99% light absorption). In that case basic principles might at first sight suggest that the fading would be zero order at the start gradually rising to first order as dye fades and light absorption decreases. In practice however this is not found.

As explained above, on account of the continual change of light intensity through the depth of the dyed material even in the most heavily

dyed materials one would expect a slow first order fade instead of a zero order, at the start, and indeed this does seem to occur in practice. If larger particles are present as well as monodisperse dye, they will fade more slowly than the latter, and tend to give zero order. (39) This explains why in practice first order fade is followed by zero order (Type II) and not the other way round.

Whether in fact the relative fading rates of successive layers of dye in a film assemblage show the above suggested differences, it was desired to examine in more detail. Thus, although monodisperse dye, which is freely accessible to light, would always fade by first order, the converse is not necessarily true, i.e. a first order fade, even if it occurs throughout the whole fading process, until all dye is decomposed does not necessarily imply that the dye is monodisperse; it might be present as small aggregates. This would explain why Daruwalla² (96) obtained first order fading for a disperse dye in hydrophobic substrates, even though there is good reason to believe that such dyes are not entirely monodisperse. (Merian⁽⁹⁷⁾, also suggested that disperse dyes are monodisperse; his evidence is based on results obtained from electron microscopy and x-ray technique).

Fading of dyes in oriented and disoriented polyester films

It was suggested⁽²⁾ that on polyester fibres the anomalously high^a light fastness observed with many disperse dyes compared with their

fastness on cellulose acetate is due to a purely physical effect, viz., retardation of fading by the low rate of diffusion of moisture to the site of fading ("diffusion-restriction" effect). In the case of polyesters it has been shown that the dye in disoriented films fades quicker than in oriented ones, which supports the hypothesis, since moisture diffusion must be more rapid in the disoriented substrate. Previous tests in this laboratory, using polyester substrates showed that fading is more rapid under damp than dry conditions and at the x-band (monomer) than at y-band (aggregate) wavelength. It was planned to check these observations independently, with newly prepared films, in view of recent suggestions elsewhere that high fastness on polyesters is due to physico-chemical effects of interaction between dye and substrate molecules. (14)

EXPERIMENTAL

Sources of irradiation

(a) The daylight being very slow^{in action} and highly variable in intensity could not be used as a fading agent (in most cases) for the experimental work. Hence an artificial light source, a General Electric "Osira" high pressure mercury vapour lamp of 400 W. was used. It had the appropriate choke in series, but no condensor. It emits light at a constant rate over long periods, and has low running cost, and it requires virtually no attention. The lamp is held in a porcelain lamp-holder screwed to a wooden board at the base and surrounded by a cylindrical sheet aluminium screen (17" diameter x 15" height), fitted at vapour stream level with a $\frac{3}{4}$ " wide aluminium shelf, on which the patterns are rested during exposure (Fig. 4). The source of illumination is a vertical incandescent vapour, hence the intensity of emission was relatively constant in any lateral direction, but even then the patterns were always transferred to different places around the shelf during fading to give a uniform fading effect. Details have been published from this laboratory in earlier papers. (36)

The lamp has a weak continuous spectrum as a background with a number of superimposed strong monochromatic bands. The five major emission lines in its spectrum are at 3650Å, 4047Å, 4358Å, 5461Å and 5780Å.

The air temperature within the screen was found to be constant, for continuous running at 56°C.

Fading in most cases was done either by keeping the films in between two clean and dry glass plates or two metallic aluminium slides having a cut area, so as to expose the film openly to the source of light.

(b) Some of the samples have been faded in the "Xenotest" (xenon arc lamp)⁽⁹⁸⁾, but these were done at other laboratories.

Measurement of fading

1. The degree of fading in most cases was determined as the decrease in optical density measured at the wavelength of maximum absorption of dye under investigation. According to the Lambert-Beer law, the optical density varies with the concentration in a linear manner in the case of a transparent medium if the thickness is constant, provided that no changes occur in the absorption properties of the solute due to alteration in degree of association and aggregation (Vickerstaff).

Most of the measurements were carried out on the Unicam SP 500 and Unicam SP 600 spectrophotometers, in each case using a "blank" film since the substrates give a positive optical density reading due to reflectance from film and glass surfaces and a certain amount of film absorption in the near ultra-violet.

The characteristic absorption curves ^{for} ~~from~~ some dyes in substrates were determined in the UV and visible range on a Perkin-Elmer automatic spectrophotometer (model 137).

2. In some cases the fading was judged visually by the International standards Organisation Light Fastness Test. This is an empirical test in which a series of eight standards, each consisting of a single blue

dye on a wool substrate, is exposed to light simultaneously with the dye under test.

3. Fading was also measured by directly measuring the percentage reflectance of the dyed patterns (poplin) on the Unicam SP 500 instrument with the special attachment provided. The reflectance increases with the decrease in dye concentration at the waveband of minimum reflection.

The calculation of relative fading
rate from fading curves

The initial fading in a large number of cases was found to be irregular, which is assumed to be due to purely physical changes, perhaps to some form of rearrangement of dye particles occasioned by heat and some loss of moisture. Consequently, the decrease in concentration (as optical density) was measured over an interval of time, t , from D_1 to D_2 , (see Fig. 5) being taken from the first suitable point on the fading curve after the dye assumes a steady rate of fading. The time for equivalent fade t_F was taken as time of exposure, calculated on the mean of fading between D_1 and D_2 , required to give a convenient (10% or 5%) decrease in value of optical density. The value of t_F is obtained for a number of optical density values and is then plotted on a log/log. graph with optical density as x-axis and t_F ^{as} ~~and~~ y-axis. The curve passing through these points, usually a straight line, is referred to as a CF curve as already mentioned.

Mounting and exposure of dyed films

The dyed films are cut to fit the cell holder of the spectrophotometer and for protection and support are sandwiched between two pieces of photographic glass plates (or metallic plates having a cut space) cut to the same size. In the normal cases of fading the film slides are then rested on a shelf encircling the inside of the aluminium shield.

Dyeing of Cellophane and gel-Cellophane

Films with reactive dyes

The dyes used were the usual commercial samples. The Cellophane films were first washed with Lissapol N solution (4: 1000 V:V.) in water and finally thoroughly rinsed and then dried for experimental use.

The dyeings were carried out in the following ways:

(a) The film was wound round the glass rod frame (~~Fig. 1~~) which was rotated at a constant speed by an electric clock motor. The film along with the frame was dipped into the dyebath contained in a beaker. The liquor ratio was kept the same in all the dyeings of this type.

(b) The films were dyed in smaller dyebaths in large test tubes without any stirring device. The stirring was done by manually shaking the tubes after certain intervals. This was done to have better exhaustion, on account of the smaller liquor-to-goods ratio.

(c) Some dyeings were made by the author at M/s. Farben Fabriken Dayer A.G., Leverkusen, West Germany, by the thermo-fixation process, which will be described later on.

The following reactive dyes were used in this work :-

1. Procion Brilliant yellow 6 G.S. (I.C.I.)
2. Procion Blue M3GS (I.C.I.)
3. Procion Brilliant Red M-5B.S. (I.C.I.)
4. Procion Brilliant Orange M-GS (I.C.I.)
5. Procion Brilliant Blue H7G. (I.C.I.)
6. Cibacron Scarlet 2G. (Ciba)
7. Remazol Red 3B. (Hoechst)
8. Remazol Yellow RTN (Hoechst)
9. Remazol Brilliant Blue R (Hoechst)
10. Levafix Brilliant Blue E.B. (Bayer)
11. Levafix Brilliant Blue E.R. (Bayer)
12. Levafix Brilliant Yellow E-3G (Bayer)
13. Drimarene Turquoise x-G. (Sandoz)
14. Drimarene Yellow x-R. (Sandoz)
15. Drimarene Discharge Orange x-3IG. (Sandoz)

For every dye, two sets of dyeings were made, namely :-

1. Fixed dyeings i.e. chemically combined with the cellulose during dyeing under alkaline conditions.
2. Unfixed dyeings i.e. adsorbed by the fibre by physical means only, without chemical combination between the dye and the fibre; obtained either by keeping the bath at pH5, or by hydrolysing the dye prior to dyeing of cellulose.

The fixation of the dye, i.e. the extent to which the dye has chemically combined with the fibre, was tested by the following procedures⁽⁹⁹⁾, as the dye could not be removed from the substrate.

- (a) The dyed pieces were boiled for 14 min. in Lissapol N (1:500, v/v.) and then rinsed well and dried. Then the fibre was treated for 4 min. at the boil in (b) to (e), in succession, rinsing the fibre in distilled water after each treatment --
- (b) a mixture of glacial acetic acid and ethanol (1:1v/v);
- (c) 15 ammonia solution (sp. gr. 0.88; 10 cc/l);
- (d) a mixture of dimethylformamide and water (1:1, v/v);
- (e) dimethyl formamide.

In general, the fixation was tested either as mentioned in (a) above or by boiling in one of these aqueous solutions: dimethylformamide, cetyl trimethyl ammonium bromide, and pyridine and in every case the dye did not come out of the substrate, thus proving that it has chemically combined with the film or the substrate.

Precion Dyes

Brilliant M-6S

The dyeings of Precion/Orange/and Brilliant Blue H7C dyes on Cellophane and gel-Cellophane were made in the following ways, but the procedure adopted for the dye was the same for both fixed and unfixed dyeings in one test or experiment.

Fixed Dyeings

- (1) The bath was set at 20 to 30°C with the required amount of

dyes (according to the depth of shade) and 30 gm/litre Glauber Salt (or Sodium Sulphate), to give a total liquor in the dyebath of 200 c.c., then the Cellophane or gel-Cellophane film mounted on the glass frame, was placed in the bath, and the test run for 30 min. and then, 15 g/litre of sodium carbonate was added. The test was then run for another 60 min. (pH 10.5). After that the temperature was raised, (according to requirement for hot or cold dyeing types of Procion dyes), and the dyeing continued for a further 30 min., after which the film was taken out and washed as follows: first, with cold water and then with hot water up to 80°C., then in a detergent solution at about 85-100°C. with Lissapol N (2 parts/1000 by volume) for 15 min.; finally with hot water and with cold water successively.

Unfixed Dyeings

The bath was started in the same way as for fixed dyeings, but the dyeing at 20-30°C, was continued for 90 min. and then the temperature was raised (as required for hot or cold dyeing types of Procion dyes), and the dyeing was continued for 30 min. without any addition of soda ash. After dyeing the film was washed with cold water and then with warm water and finally with cold water again.

Note:

(a) Afterwards, as the depth of shade on unfixed dyeings was very weak (i.e. most of the dye washed away), in some cases the films were washed only with cold water or were not washed at all. But this does

not affect the fixation of dye, hence the change is of no importance.

(b) In some cases the amount of Glauber salt was increased to give better adsorption of dye and thus deeper shades, but this was also found not to affect fixation.

(ii) A number of pieces of film were immersed in a relatively large volume of dye solution of a suitable concentration containing 30 g./litre of sodium chloride but no alkali. They were left for approximately 24 hr. at room temperature with a constant slow stirring. Then the pieces of film were removed, surplus dye solution shaken off and then some of them were rinsed with cold water and dried. These were the unfixed dyeings. The remaining pieces were immersed in a saturated solution of sodium chloride containing 0.1N sodium carbonate for 2 hr. After well rinsing in cold water the film was treated with 50% ethanol-water to remove any loose dye remaining and finally rinsed again in water. These were the fixed dyeings.

Remazol Dyes on Cellophane

The procedure applied to all the Remazol dyes was as follows:

Fixed Dyeings

The dye bath was set at 60°C. with Glauber's salt anhydrous (30 g./l. and dye, then the Cellophane sheet mounted on the glass rod frame was lowered into the bath and run for 20 min., after which, 2 g./l. sodium bicarbonate was sprinkled in, and 0.5 c.c./l. sodium hydroxide (0.6 c.c. of 10% w/v solution) was added, then after 20 min. and 40 min. further portions of sodium hydroxide, 1.5 c.c./l. and 1 c.c./l. respectively

were added; dyeing was completed after a further 40 min. in the same bath. Then the dyed film was washed with, successively, running cold water, acetic acid (to neutralise), hot water (80°C), 1g./l. Lissapol N solution at boiling point, and finally, with cold water.

Unfixed Dyeings

The bath was set at 60°C with dye and 30 g./l. Glauber Salt, the mounted film being put into the bath and dyeing continued for 100 min. The film was then washed with cold water.

Sibacron Dyes on Cellophane

Fixed Dyeings

The dye bath was set at 40°C , with dye, one-third of the required amount of Glauber Salt, and the dyeing started. Then the temperature was raised to $70-80^{\circ}\text{C}$, in 45 to 60 min., during which period the total amount of salt required was added in three portions to a total of 40g./l. After this 20g./l. of dissolved trisodium phosphate (crystalline) was added in two portions, and the solution kept for 45 min. at $70-80^{\circ}\text{C}$ for effecting the fixation. Then the film was washed thus: the unfixed dye was removed by soaping at the boil for at least half an hour with 2g./l. Lissapol N solution, then the film was rinsed thoroughly with warm water and then with cold water.

Unfixed Dyeings

The bath was set at 40°C with, dye and Glauber salt (one third of total amount), and the dyeing was started. The temperature of the bath was raised to $70-80^{\circ}\text{C}$ in 45-60 min. during which period the total amount of salt required was added in three portions, the amount used being 50g./l

The dyeing was carried out for another 60 min. at 70-80°C. A final rinse in cold water was given.

Levafix Dyes

The bath was set at 40°C with the required amount of dye and 50g./l. of Glauber Salt (calc.). The dyeing was carried out for 3 hr. Then one half of each piece was washed with cold water and then dried; they were the unfixed dyeings.

The remaining pieces were treated further, in a saturated solution of Glauber Salt and 20g./l. of sodium carbonate, for 2½ hr. These were the fixed dyeings. These were washed first with cold water, then with hot water at 80°C, followed by soaping with Lissapol N (1:500, w/v) for 15-20 min.; finally hot water and with cold water successively.

Brimarene Dyes

Fixed Dyeings

The dyebath was set at 40°C with the required amount of dye and 7g./l. of Glauber Salt. The pH was maintained between 10 and 10.5 with sodium hydroxide. The bath was raised to near boiling in 1 hr. and kept at it for 1½ hr., this was followed by the usual washing-off treatment with Lissapol N (1:500 w/v).

Unfixed Dyeings

These were dyed in exactly the same way as the fixed ones, except that the pH of the dyebath was maintained at 5.0 throughout.

Typical unfixed dyeings

Some of the unfixed dyeings were made by hydrolysing the dye first

by keeping it overnight and then boiling it for an hour or two at pH 10.5-11. The dyeing was carried out at pH 10.5-11 like a fixed dyeing.

Dyeing of mercerised and unmercerised cotton and viscose rayon yarn with Levafix Brilliant Blue E-B

The goods were entered at 40°C. and ^{10g/l} Glauber Salt (calcined) was added (Table 3,4). After 60 min. the required amount of sodium carbonate was added in three portions to fix the dye. The dyeing was further continued for 90 min. This was followed by a hot rinse, then soaping with Lissapol N (1:500 v/v) at boil for $\frac{1}{2}$ hr., rinsing with hot and then cold water.

Dyeing of cotton poplin by thermosol process

The dye was padded from solution at 20-25°C on to the poplin, which was then dried at 80-100°C; the thermofixation of the dye was brought about at 150°C.

The padding liquor for fixed dyeings was prepared with the required amount of dye, 150 g./l. of urea and 10 g./l. of sodium carbonate (calcined). After dyeing these were rinsed with cold and hot water and then soaped with 1-2g./l. of Levapon TH ^(Bayer) /highly concentrated for 10-20 min. at 98°C. Finally rinsing in hot and cold water was carried out.

In the case of unfixed dyeings the padding liquor used was without urea and sodium carbonate.

In some cases only half the amount of urea and sodium carbonate was added to the padding liquor. These dyeings were given the same washing and soaping treatment as in the case of fixed dyeings having full amount

of urea and sodium carbonate.

Some of the unfixed dyeings were washed with cold water only, while some of them were left totally unwashed before being tested for their light fastness.

Preparation of Cellofas A films

(methyl ethyl cellulose)

A 4% aqueous solution of Cellofas A (I.C.I.) was prepared cold by stirring continuously for 22 hr., then centrifuged for one hour to deposit the fibrous material. The supernatant liquor was collected for use in making films. In every case of making films with Cellofas A, 17 c.c. of this solution was mixed with 10 c.c. of the dye solution alone or with other solutions e.g. glucose or methanol in this ratio, and was poured on to "subbed"* photographic glass plates all of the same size for one test. The plates were levelled on a sheet of plate glass on a metal frame heated below by four carbon lamps of 100 w. each. Quite uniform films were obtained by this method, but even so care was taken to use the best portion of the film for making slides for fading.

* Footnote:

"Subbing" refers to a treatment with a silicate solution, followed by drying, given to the plates used in this work (kindly supplied by Ilford Ltd.), to ensure the adhesion of the gelatin emulsion in subsequent processing.

The light fastness of Procion dyes

66

with and without glucose yes

with and without glucose

Dyes used:

1. Procion Brilliant Yellow 6 GS
2. Procion Brilliant Red M-5BS

Procedure:

0.2 c.c. of each dye from solution of 1% strength was kept in two test tubes separately. In one, 0.8 c.c. of 2% solution of glucose (more than four times the molecular proportion of the dye) was added and then all the solutions were made up to 10 c.c., thus one set of two tubes contained dye + glucose in water at pH 10.5, and the other set contained dye in water only at pH 10.5. All the solutions were kept overnight for completion of the reaction. Then films were made from 8.5 c.c. of the Cellophas A solution mixed with 5 c.c. of each of the above solutions respectively. These films were later exposed to light to study their fading (Fig. 6.7).

The light fastness of reactive and direct dyes

dyed with glucose at pH 10.5 and 5.0

Dyes used:

1. Procion Brilliant Yellow 6G
2. Remazol Red 3B
3. Chlorazol Fast Pink BKS
4. Procion Brilliant Orange M-G.S.

Procedure:

0.2 c.c. of each dye solution (1% strength) was kept in two tubes separately. To both tubes 1.6 c.c. of 1% solution of glucose was added and then all the solutions were made up to 10 c.c. One portion of solution of each dye was made to pH 10.5 by the addition of sodium hydroxide, and the other to pH 5.0 by the addition of acetic acid. All the solutions were left overnight to complete the reaction. Then a film was made with Cellofas A solution as before. These films were exposed for fading (Fig. 8,9).

Light fastness of hydrolysed and unhydrolysed reactive dyes

Films of the same depth of shade with Cellofas A were made as described, with two sets of each dye; one, with hydrolysed dye, i.e. at pH 10.5; and the other with unhydrolysed dye, i.e. at pH 5. The dyes were hydrolysed by keeping for 99 hr. in aqueous solutions at pH 10.5.

Dyes used:

1. Remazol Red 3B.
2. Remazol Yellow RTN
3. Procion Brilliant Yellow 6G.

Reacting methyl alcohol with reactive dye before dyeing Cellonphane

Methyl alcohol was reacted with dye (Procion Brilliant Yellow 6G) at pH 10.5-11.0 (alcohol being in excess) at 20-30°C. for 1 hr. and then the reaction was allowed to continue at 40-45°C. for another 1 hr., after

which the solution was cooled down to start the dyeing of Cellophane in the usual way. In the case of Cibacron Scarlet 2G alcohol was again taken in excess and the bath was set at 40°C and then Glauber salt (as usual in three portions) was added; the temperature was raised to 70-80°C in 45 min. and then trisodium phosphate (crystalline) was added in two portions. The treatment was continued for another 45 min. then Cellophane was dyed in the usual way.

Effect of sodium hydroxide on direct dyes.

The dye used was Solar Green BL. (GY). The bath was set at 30-40°C. with 10% Glauber Salt (on the weight of Cellophane film), then the temperature was raised to 85-90°C and kept thereat for 1 hr. After intervals of 30 min. each, a total of 20% Glauber Salt was added in two portions. The dyeing was continued for a further 30 min. and the temperature was maintained throughout at 85-90°C.

The other set of dyeings of Cellophane film were dyed as above but with 10% sodium hydroxide ^{on weight of film} (to obtain pH 10.0) added to the bath after 30 min. the temperature reaching 85-90°C.

Difference in light fading of direct dyes (having a free chlorine atom at the triazine ring) with and without alkali

Dye used: Direct Brilliant Pink G (C.I. Direct ^{Red} 71)

Procedure:

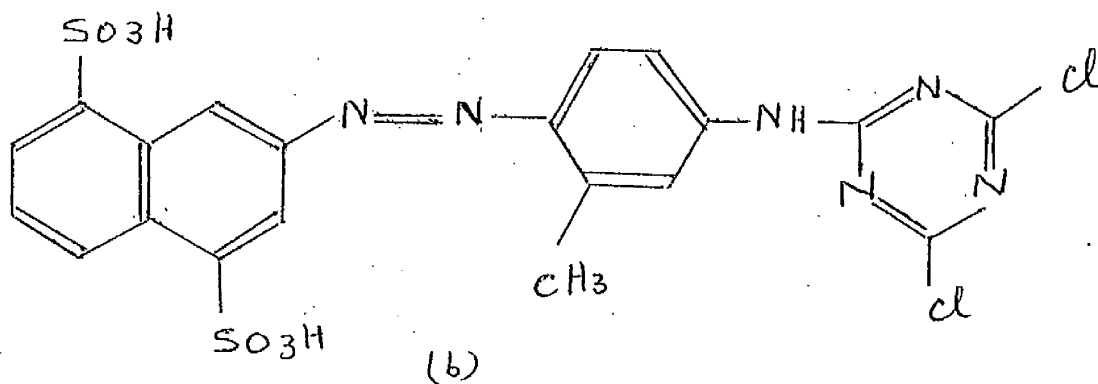
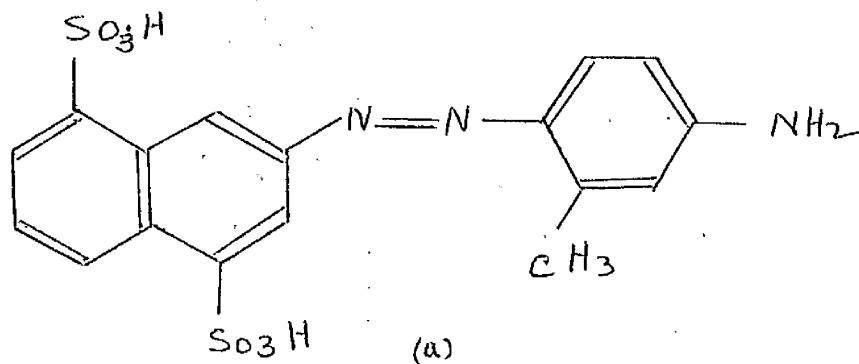
The dyebath was set at 50°C. with the required amount of dye and

16% Glauber salt. It was raised to boil in 20 to 30 min. and kept at boiling for 60 min.

In the case of dyeings with alkali (pH 10.5), the sodium carbonate (1% on the weight of Cellophane) was added to the bath in the beginning.
Light fastness of unfixed dyeings after
different times of washing

The unfixed dyeings from the previous dyeings of Procion Brilliant Yellow 6G and Procion Brilliant Orange M-GS were given different times of washing with cold water. Then their light fastness was tested (Fig. 10).

Irradiation by mercury vapour lamp of two dyes having
the same ^{structure} base but an additional triazine ring
attached in one (reactive dye)



The dyes (a) and (b) were irradiated in an aqueous solution and their absorption curves (Fig. 11-14) were taken before and after irradiation to discover if any chemical change had taken place.

Fluidity measurements of fixed dyed Cellophane film before and after fading

The fluidity of fixed dyed Cellophane film was measured before and after fading in cuprammonium solution by "Shirley" X-Type viscometer. (So far no useful results have been obtained).

Fading of mercerised cotton, unmercerised cotton and viscose rayon yarn dyed fixed and unfixed, tested by xenotest and fadeometer

The fibres dyed in the yarn form with reactive dyes, both fixed and unfixed.

Some of the unfixed dyeings were not washed at all, while the others were washed with cold water only. But all the fixed dyeings were given a usual soaping treatment to remove the hydrolysed dye sticking loosely to the fibre.

Detection of dye aggregates by x-ray photography

The reactive dye having phthalocyanine base (Procion Brilliant Blue H7G) was purified⁽¹⁰⁰⁾ first, and then applied on the Cellophane film by the usual procedure for a fixed or unfixed dyeings. Then x-ray photographs (Fig. 15-20) were taken of the original cellophane film, and the fixed and unfixed dyed Cellophane films, separately, to see if it is possible to detect the presence of aggregates in fixed and unfixed dyed Cellophane film.

Qualitative examination of dichroic effect in

fixed and unfixed dyed Cellophane film
Qualitative examination of dichroic effect in

fixed and unfixed dyed Cellophane film and undyed Cellophane film by

a polarising microscope, but both the fixed and unfixed dyed Cellophane films did not show this effect either in deep shades or in weak shades. This suggests that the dye is aggregated rather than oriented as a monolayer on the cellulose molecules. Dyes used were:

(a) Procion Brilliant Orange M-GS

(b) Cibacron Scarlet 2 G.

Irradiation of dye solutions by mercury vapour lamp

The source of irradiation was a 125 W. Osira high pressure mercury vapour lamp which was stabilised with a capacitor and choke. It was kept at a distance of 6 inches from the dye solution. The absorption spectra (Fig. 20, 22) of the dye solutions were taken before and after irradiation.

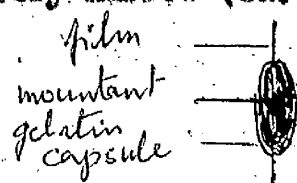
Electron Microscopy

To detect the presence of dye aggregates in the dyed films, this technique was used by the following procedures.

1. Section cutting by microtome of the dyed Cellophane film

The dyed Cellophane film was embedded in a mountant in a gelatin capsule to enable it to be cut by the microtome. The mountant was prepared by mixing first Araldite epoxy resin 6Y 219 (5g.) and Araldite hardener HY 1219 (2.5g) at room temperature; stirring thoroughly. Then Araldite accelerator DY 219 (0.15g) was added, stirring it thoroughly into

the resin-hardener mixture until a uniform colour was obtained. The very narrow (ca. 0.5mm.) strip of the film was passed through small



houses in top and bottom sections of the gelatin capsule which was then filled with

the mountant. The whole assemblage was left for 24 hr. at temperature between 30-40°C in an oven, and then sections cut at right angles to its length, by microtome, after the gelatin capsule had been torn away, and the solid mass of embedding material had been trimmed by razor blade to a rectangular cross-section, with the aid of a microscope.

A glass knife, which was prepared by sharply cutting a thick glass strip, was used for section cutting. The mountant and the knife were so adjusted that the edge of the knife should be parallel to the edge of the rectangular head of the mountant. This was necessary to get good

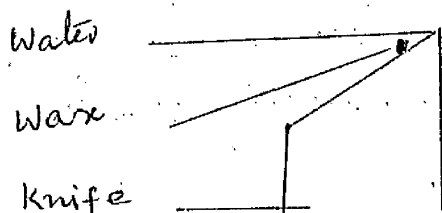


Fig. 23

sections. At the sloping edge of the knife (Fig. 23) a little wax was put and a drop of water was kept there, to make the sections

float, thus assisting removal from the knife edge. Unfortunately the results were unsatisfactory because the sections were too brittle and broke before they could be tested. This matter was not proceeded with. Hence we adopted the following technique.

Making very thin cellulose film for electron microscope

This was first done by making cellulose triacetate film and then saponifying it to get pure cellulose film.

(a) Preparation of cellulose triacetate film

Cellulose triacetate film (0.5 gm.) was dissolved in 100 c.c. of methylene chloride. The solution was stirred for 3 hr. to give a very homogeneous solution at room temperature, in a wide test tube, which was

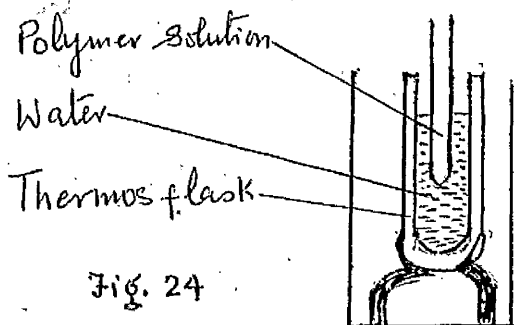


Fig. 24

surrounded by water in a Thermos flask

(Fig. 24) to keep it at a constant temperature. After this the polymer solution was allowed to stand for $\frac{1}{2}$ hr. to come to room temperature.

(b) Preparation of glass slides

New glass slides were used. Their surfaces were thoroughly cleaned with a solution of Lissapol N or D (Paste). Then they were rinsed with a large amount of water and all the surfaces were rubbed with the fingers to remove any film of wetting agent that may have remained. The glass was then wiped dry with a clean, absorbent lint free cloth. Afterwards, the surfaces of the glass strips were conditioned by immersing the glass (with a string sling) under methylene chloride for 30 min., and then allowed to dry in air. This treatment gives a uniform surface condition on the glass slides prior to dipping in the polymer solution. This treatment (a) seems to allow time for the dissipation of any static charge produced by rubbing the dry glass slides with a cloth and (b) produces a reasonably constant and reproducible moisture condition on the glass surface.

Casting of film

The slides were lowered one by one by hand into the polymer solution at room temperature, until each was immersed up to three-quarters of its length into the solution. The slide was allowed to remain in the polymer solution for 10 sec., and then was allowed to dry in air. The entire procedure was performed in a closed small room, this being a significant controlling factor in the evaporation rate of the solvent from the glass.

Conversion of cellulose triacetate to cellulose film

The cellulose triacetate film thus obtained was saponified by 1.0N sodium hydroxide solution cold for 24 hr. Film thus obtained was dyed with the reactive dye.

As the films thus obtained showed a great amount of porosity (Fig. ^{25,26}), other films obtained by the same method were saponified by 0.1N sodium hydroxide in a saturated solution of sodium chloride for 48 hr. Sodium chloride was used to prevent swelling of the regenerated cellulose film.

To recover the films a beaker was filled up to the brim with water. The slide having the polymer film (cellulose or cellulose triacetate) was dipped into the water. After scoring of the edges of the glass slide with a needle, the polymer films were floated off the glass slides on to the surface of the water.

Dyeing of films for the electron micrograph

Dyeing of triacetate films was performed in a solution of 0.5g. of dye (Duranol Violet 2 R 300 Powder Fine) in 150 c.c. of water in a beaker, by the normal procedure.

Cellulose films were first placed in a dye (Procion Brilliant Orange M - GS) solution of arbitrary concentration at pH 10.5, to check if they could be dyed. The result was positive. Then films were dyed at pH 10.5 in a solution of 20 g. of dye in 300 c.c. of water to give the fixed dyeings of Procion Brilliant Orange M-GS and Levafix Blue E.B. The unfixed dyeings were made with a similar solution at neutral pH, but the dye came out when it was kept in water.

Preparation of polyester films for electron micrographs

The same apparatus and procedure was used here as in the case of cellulose triacetate films. But 0.8g. of polyester film (Melinex) was dissolved in boiling N-methyl-2-pyrrolidone (100 c.c.). Then the films were prepared on the glass slides by dipping them into the solution, as usual.

These films could be dyed by the usual procedure but could not be taken off the slides, as they were very brittle and broke up too easily. Hence, it was not possible to take their electron micrographs.

The Cellophane film was dyed with Solar Green BL. 1r.

Dyeings were started at 30-40°C with 10% Glauber salt and dye in the bath. The temperature of the bath was raised to 85-90°C and kept for 1 hr. After $\frac{1}{2}$ hr. at 85-95°C another 10% of Glauber salt was added.

Again after 1 hr. another 10% of Glauber salt was added and the dyeing was continued for another $\frac{1}{2}$ hr. *to ensure levelness.*

These dyed films were irradiated for some time and then kept in dark for some time; this procedure was repeated throughout the fading period (Fig. 27).

Difference in fading of direct dyes in glass slides and in open exposure

Cellophane film was dyed with the following direct dyes in the usual manner, Chlorazol Sky Blue F.F. (C.I. 24410), Durazol Flavine BS (C.I. 29025), and also with an insoluble azo-dye prepared from naphthol AS in the laboratory.

The same direct dyed Cellophane film was exposed freely in air and the other was sandwiched in the usual way between glass slides (Fig. 3). Both the slides were irradiated together under similar conditions. The freely exposed film was fixed over a cut-out in an aluminium strip, cut to enable use in the spectrophotometer. (see Fig. 28, 29, 30, 31(b), 32(b)).

2. Fading of direct dyes having glass slide and metal slide only on one side in each case

This time the film was exposed to light by supporting the film only by one glass slide but reversing the system, i.e.,

- (a) in one case the glass slide was towards the lamp and the film at the back of the glass slide;
- (b) in another case the film was towards the lamp and the glass slide at the back of the film;

(c) a metal slide was used as described to hold the freely exposed film.

3. Fading of direct dyes in glass slides with and without an air gap in between the two slides. (Fig. 31(a), 31(c)).

The glass slide having no air gap was the same as used in normal experiments. The one having an air gap was formed by putting a packing washer of paper in between the two slides and the film so as to leave some space for the air to pass through.

4. Difference in temperature rise between glass and metal slides on exposure to the lamp. (Fig. 33)

A calibration curve was drawn of millivolts against temperature with a thermocouple (Fig. 34).

The difference in temperature rise between the two different types of exposures of the films (glass and metal slides) could thus be measured.

Preparation of gelatin film

A 6% aqueous solution of gelatin, of pure "inert" photographic quality, was mixed with the required amount of dye solution and poured on to a "subbed" photographic glass plate on a screw-levelled platform, then dried slowly by heat in still air to give a film of uniform thickness. This was the plain film with smooth surfaces. (Fig. 35)

Gelatin film having one or two rough surfaces

This was prepared by treating the film as above but on a plate either one or both surfaces of which had been roughened by Carborundum powder (Fig. 35):

Films having different grades of roughness

To achieve different grades of roughness (to imitate the different grades of wool) in the gelatin films, different grades of Carborundum powder were used, namely Grades 80, 220, and 600. The dyes used were, Acid Magenta A150 and p-nitroaniline \rightarrow R-acid (Na salt).

Dyeing and drawing the fading rate curves

of direct dyes

The following direct dyes were dyed each in two different depths and then exposed to light and their fading rate curves drawn.

1. Chlorazol Sky Blue T.F.

This was applied to Cellophane in a warm liquor (40°C); the temperature was raised to boiling point in half an hour. Glauber salt (20%) was then added in three portions and the solution kept boiling for 1 hr.

2. Durazol Flavine R.S. (C.I. 29025)

The Cellophane was dyed in warm bath having dye only in the solution. The temperature was raised to near boiling in half an hour. Glauber salt (10%) was added to promote exhaustion, and the bath kept at boiling point for 45-60 mins.

The same procedure was applied to all the following dyes:

3. Calcodur Yellow R.L. (C.I.29025)
4. Calcodur Orange 5G
5. Calcodur Violet N (C.I.22570)
6. Calcodur Blue 6G
7. Calcodur Blue A G.L.

The y/x ratios of the following dyes were taken in Gel-Cellophane and Cellophane, both in dry and wet state and in de-ionised water.

(Table 5)

1. Chlorazol Sky Blue F.F.
2. Chlorazol Azurine G.S.
3. Benzopurpurine 4B.

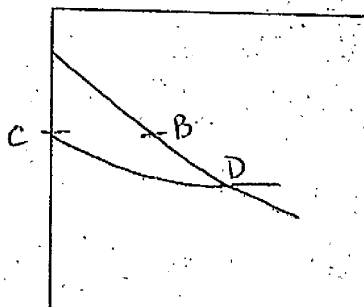
Dyeings were performed by the method already described before.

Fading of Chlorazol Sky Blue F.F. and Duranol

Violet 2 R 300 on Cellophane and Polyester films

The Cellophane and polyester films were dyed with Chlorazol Sky Blue FF and Duranol Violet 2 R 300 respectively by their standard method.

They were kept in a group of three films together for fading. Their readings of optical density were taken first, of every film separately and then in a group together.



A number of fading curves of different dyes were examined and their fading rates from equal concentrations were compared, e.g. rate of fading from B to D was compared with rates of fading from C to D (Fig. of the curves examined).

Preparation of polyester film

Disoriented polyester film was made by dissolving 0.8g. Melinex film (I.C.I.) in boiling N-methyl-2-pyrrolidone (100 c.c.), and pouring it, as hot as possible, on to glass plates, then drying slowly by heat in still air to give a translucent film.

"Melinex" film (thickness 0.003") was used to represent an oriented fibre. Both oriented and dis-oriented polyester films were dyed in a domestic pressure cooker at 120°C. for 60-75 min. with the same liquor ratio, the dyes used being serisol Brilliant Violet 2R. and Duranol Violet 2K 300.

Moisture contents of the disoriented polyester film during exposure were measured by weighing immediately after long exposure 74 hr. in the fading lamp, and after drying in the oven to constant weight at 120°C. Result: weight lost in oven = 1.2%; weight lost during fading = unmeasurable; both referred to original air-dry weight.

Disorienting polyester film by boiling

The Melinex film was boiled in water under 115 lb. pressure at 120°C for 3 hr. (pressure cooker) to obtain some degree of dis-orientation then dyed as above and tested for light fastness under dry and humid conditions.

Fading under dry and wet conditions

All the fadings under dry conditions were done by hanging the dyed film slides (1½" high) in a tube having calcium chloride at the bottom.

The fadings under wet conditions were done by keeping some water at the bottom of the tube, the slides being hung one inch above the water level.

In all cases the slides were so arranged as to face the light source, parallel to the circumference.

Disoriented polyester film (0.005" thick), supplied by I.C.I., was used in some experiments, and it was dyed by the usual procedure.

Uptake of moisture by oriented and
disoriented polyester film

First, both the films were weighed and kept in an oven at 120°C to dry. After some time the films were taken out and kept in a desiccator for cooling, then weighed. This procedure was repeated again and again till the films reached a constant weight respectively. Then they were left in the open atmosphere to recover their moisture contents, and their weights were taken after certain intervals, till they reached a constant weight again.

Fading of Dispersol Orange A150 Powder on cellulose
triacetate, sandwiched between polyester and
cellulose triacetate films separately

Cellulose triacetate film was dyed at the boil for one hour in an open beaker containing dye solution of required strength. Portions of this dyed film were sandwiched between two polyester and two cellulose triacetate films respectively, which in turn were sandwiched between two metallic slides. All the four sides of the whole assembly were sealed

with Araldite, so that no air or moisture can get in and reach the dye
cellulose triacetate film, during fading, from the edges.

DISCUSSION

fastness of reactive dyes

Effect of dye-fibre bond strength on the light

fastness of reactive dyes

The present work was a result of Ingamells report, in which he showed that the light fastness was always higher in case of fixed reactive dyeings (Table 6), compared with the corresponding unfixed ones. The cause was explained by him as the transference of light energy from dye molecule to the fibre. Hence, the present work started with the repetition of his tests, with various dyes. Most of the reactive dyes (Fig. ³⁶⁻⁵¹) gave similar results to Ingamells', but the Remazol dyes (Fig. 52-56) did not show any difference in the light fastness of fixed and unfixed dyeings. Similarly, very little or no difference could be seen in the case of Levafix Brilliant Blue E.B. (Fig. 57, 58) and Drimarene Turquoise K-G (Fig. 59) (this is still under test for fading). These results cast some doubt upon the explanation given by Ingamells.

To ascertain the effect of alkali on the light fastness of these dyes, a direct dye was applied to Cellophane film both under normal dyeing conditions and under alkaline conditions like a fixed dyeing of a reactive dye. On irradiation of these dyeings it was found that the light fastness was unaffected (Fig. 27).

Glucose being similar to cellulose in its chemical constitution was expected to form a covalent bond with the reactive dye and thus should increase the light fastness, which it did (Fig. 6, 7, 8) when tested in

casting from

aqueous solution of dye; but this might perhaps have been due to the formation of larger aggregates in the glucose solution than with water only. A further test was therefore made in which reactive and direct dyes were irradiated after casting together with Cellofas as film in the solid state. In one case application was in presence of glucose at pH 10.5, the dye being expected to react with glucose under these conditions, and at pH 5 where it should not react. Again it was found that Procion Brilliant Yellow 6G showed the better light fastness after application at pH 10.5 (Fig. 7, 8), but Remazol Red 3B and a non-reactive direct cotton dye, Chlorazol Pink BKS, did not show any difference. Procion Brilliant Orange M-GS, a highly substantive reactive dye showed better light fastness in the films cast at pH 5 than at pH 10.5 (Fig. 9, 60). This is rather difficult to explain as it could not be due to the dye being hydrolysed at pH 10.5. The results were reproducible and it is difficult to explain why Procion Brilliant Yellow 6G behaved differently. ^{on cellophane (Fig 38) (cf. Fig 41)} Next, the dye was hydrolysed first and then either Cellofas films were prepared by casting or Cellophane films were dyed and their light fastness was compared with those films dyed with unhydrolysed dye. No difference was found in the case of Remazol yellow and Remazol Red dyes, while in the case of Procion Brilliant Yellow 6G and Procion Orange M-GS, the light fastness was better in the case of unhydrolysed ^{and fixed} dye (Fig. 42, 61, 62). In the case of Cibacron Scarlet 2G the light fastness was highest in the case of unfixed dye (Fig. 63) and lowest in the case of fixed dye, but this might

perhaps be due to mere concentration effects.

A direct dye having a free chlorine atom on the triazine ring shows better light fastness when dyed at pH 10.5 than when dyed with normal dyeing procedure (Fig. ⁶⁴⁻⁶⁵). It was also found that the dye was chemically combined with the Cellophane as it could not be extracted out of the dyed film either with boiling soap solution or with pyridine. Remazol dyes however gave different results (Table 7). In a private communication Hoechst-Cassella Dyestuffs Ltd., have suggested that the equal or sometimes higher light fastness in case of unfixed Remazol dyes on mercerised cotton is due to the higher dye concentration on the unfixed dyeings. This agrees with our explanation in the case of Cibacron Scarlet 2G (Fig. 63 and Table 8).

It was shown by Rahman⁽⁴²⁾ in this laboratory that in the absorption spectra of reactive dyes on regenerated cellulose the y/x band extinction ratio increases with the increase in concentration. This fairly certainly indicates that these dyes exist in an associated form in cellulose. Baxter et al.⁽³⁶⁾ also reached the same conclusion by studying the fading rate curves. In the present work fading rate curves for the reactive dyes have been obtained as explained earlier, and these curves appear from their shape to show the presence of dye aggregates; in general these curves fall into classes 2, 3, and 4 (Fig. 6, 37, 43-46, 50, 53-59).

The absorption spectra of these dyes and the change in the height of the y -band relative to the x -band with increase in concentration, whether in solution or in solid substrate (Table ^{Fig. 65-67} 9 +) appears to confirm the

existence of aggregates, suggesting that intermolecular forces of reactive dyes are sufficiently powerful to cause aggregation even when one or both reactive points of the dye molecule are covalently attached to the fibre molecular chain. It was found that the y/x ratio increases after fading (Fig. ⁶⁶⁻⁶⁹) which should be the case if the breaking down of dye aggregates takes place during fading.

While the experiments were being conducted at the Bayer Laboratories in Leverkusen, Germany, it was found that two dyes, Levafix Brilliant Blue E.B. and Levafix Brilliant Blue E.R., show a tendency to decrease in light fastness with rise in depth of shade (Table 10). The explanation given for this was that when all the sites are occupied by the dye molecules, then any further amount of dye which goes on to the fibre is not bonded with the fibre, and thus will cause this lower light fastness. If this were true in this case then it should hold true for other dyes of this class and possibly of other classes^{oo}/well.

The tests carried out with Levafix Brilliant Blue E.B. dyed by the Thermosol process showed (Table 11 and Fig. 68,69) that the dyeings without urea and sodium hydroxide had better or the same light fastness compared with the dyeings having half the amount of urea and sodium hydroxide or the full amount of urea and sodium hydroxide required for a normal fixed dyeing. This indicates that the light fastness is probably not affected by the dye-fibre bond, as the dye should not react with the fibre in the absence of urea and sodium hydroxide. Similar results were obtained with Levafix Brilliant Red E-4B and Levafix Brilliant Yellow E-3G (Table 12,13).

It was found (Fig. 10) that the light fastness of unfixed dyeings improves with their washing times, provided the dye can survive the treatment, as most of the reactive dyes come out of the substrate during washing with cold water only. This improvement in light fastness with washing may be attributed to the fact that the dye loosely attached on the surface of the film fades much quicker than the dye inside the fibre. Light fastness results supplied by B.A.S.F. on Primazine dyes (Table 14) showed similar results.

If Ingamzells' suggestion were correct ^{the cold} dyeing Procion dyes, which form two covalent bonds with the fibre, should have higher light fastness than those of hot-dyeing type, which have single bonding, but this is not found in practice. Also the data given by the manufacturers show that the light fastness increases with concentration, except in case of Levafix Brilliant Blue E.B. and Levafix Brilliant Blue E.R., and this ^{because it seems as if here} should have not been so, as the dye-fibre bonds are reduced in strength with increase in depth of shade.

It was expected that the double covalent bonding might bring the parallel cellulose chains closer and thus compress the whole structure, thus leading to a higher specific gravity of the fixed dyed Cellophane compared with the unfixed dyed Cellophane film. Tests however did not show any difference in the specific gravity of unfixed or fixed dyeings (Table 15). Mehta et al⁽⁸¹⁾ have doubted this linking of the dye with the fibre and the observed insolubility in cup/rammonium solution of Cellophane after reactive dyeing, they attributed to the insolubility of

the copper complex of the dye. If light energy is transferred to the cellulose then the reactive-dyed cellulose might show some degradation after fading, but no reliable results could be obtained to test this hypothesis, because of the insolubilising effect.

The dyes were irradiated in aqueous solutions and in dyed films (Fig. 70-74). Their absorption spectra were taken before and after irradiation, but no evidence of any chemical change could be observed, as the shapes of the absorption spectra were the same before and after irradiation. To examine the effect of the triazine ring itself during fading, the two dyes A and B (Fig. 11-14) having the same basic structure were taken and irradiated but again, no difference was observed.

The absence of the dichroic effect in the case of the fixed reactive-dyed Cellophane films suggested that the dye is not in an oriented state and thus may be in aggregated state.

Attempts to detect directly the presence of dye aggregates in fixed and unfixed reactive-dyed Cellophane films were made (by Mr. Yousuf Zai in Fibre Science Department), but gave no useful results. The X-ray diagram of the dyestuff itself in solid form had the pattern of a well-crystallised substance (Fig. 15, 18), hence in dyeings some reflections of the dyestuff pattern were expected, and possibly these might have been different in fixed and unfixed dyeings; but no differences could be detected. (Fig. 17, 19, 20).

However, aggregates could be clearly seen in electron micrographs of reactive dyes on cellulose (Fig. 25, 26, 78-80). (Those were ^{not} dust particles as

they are absent in the case of the undyed control film (Fig. 81)). In some cases the high porosity of the cast film is very clear (Fig. ^{25,26}),
(Fig. 78,80) in others/it looks as if the cellulose film has ruptured due to the high concentration of the dye, which has drawn the cellulose chains apart. Some of the very big needle-like structures visible may be dye crystals on the surface of the film (Fig. 78) as this was not washed before taking the electron micrograph. Electron micrographs could not be taken of unfixed dyeings because the dye came out of the film in water, when kept before mounting on the grid.

A survey of the published light fastness data of the reactive dyes given by the manufacturers showed that all have higher light fastness on viscose rayon than on cotton (Fig. 82, 84) and their light fastness rises with the concentration, i.e. there is a positive slope of CF curve, ^{38-42, 49, 51 & 52).} and this was found in our own results as well (Fig. 36). This effect is good evidence of aggregation in reactive dyes⁽³⁹⁾. The only class of reactive dyes which did not show higher light fastness on viscose rayon than on cotton was the Primazine, although these do show a rise in light fastness with rise in concentration on the fibre (Table 19). The data show that the wet fastness ratings of all the reactive dyes are the same. Cellulose, which has been modified so as to increase the number of primary hydroxy-groups in the accessible region, upon dyeing with reactive dyes shows an increased rate and extent of dye uptake, and the wash fastness of the printed fabric is greatly improved.⁽⁸⁶⁾ This confirms that the dye-fibre bond is responsible for the wash fastness.

Unfortunately no corresponding light fastness data are available.

Further light fastness tests were carried out here on bleached and mercerised cotton and on viscose rayon. It was found that light fastness was highest on viscose rayon and lowest on bleached cotton (Table 16) suggesting again that the various differences in light fastness described above are probably largely due to aggregation effects.

The extent of amorphous region and porosity decreases in the order viscose rayon > mercerised cotton > bleached unmercerised cotton, and the tendency for aggregates to form inside the fibre would be expected to follow the same sequence.

Another cause of lower light fastness in unfixed dyeings might be the presence of hydroxyl groups at the reactive site of the dye molecule.¹⁰ This effect of a decrease in light fastness with the addition of a hydroxyl group was found while surveying the effect of different substituents in published data for a series of dyes of known structure (Table 17). This would explain why Procion dyes show lower light fastness in unfixed dyeings and the Remazols do not, because the former are less stable to hydrolysis and their dyeings (unfixed) would contain some hydroxylated dye.

Effect on direct dyed Cellophane fading rates of alternating irradiation and storage in the dark

The dye examined showed a constant decrease in optical density indicating fading, but on keeping in the dark the optical density increased every time. This may be due to the re-formation of aggregates

on cooling in the absence of light.

(4927)
By viewing the graph/as the whole however there is seen to be a constant fading. The changes were more in the case of the yellow peak than in the blue and the decrease in optical density on the whole was more in the case of the yellow peak than in the blue peak of the dye.

Difference in fading of direct dyes in
glass slides and in open exposures

During long exposures it was noticed that the fading is more in case of films sandwiched between the glass slides than the ones exposed openly (Fig. 28-30, 31(b), 32(b)). This can be attributed to the fact that the film in the glass slides attains a higher temperature than the one exposed openly (Fig. 33).

The more rapid fading in glass slides compared with those exposed openly in metal slides after long exposures may further be affected by the moisture and air availability, since after long exposure to light the film becomes dry and crinkled and hence some passages are formed whereby access of air and moisture (present in air) is assisted.

The films in the glass slides with or without air gap (Fig. 31(a), (b); 32(a)) show a quicker fading with gap, at first, but not in later stages. This again may be due to the more ready availability of moisture and air.

The film exposed towards the light source and mounted on a glass plate (Fig 31(b), (c); 32(a), (b)) shows more rapid fading than the film either exposed in open air (on metallic slide) or at the back of the glass slide (i.e., glass slide facing the lamp), which would be expected, because it

receives maximum light irradiation and maximum heating.

The Cellophane film dyed with the azo dye (prepared in the laboratory) was also exposed in glass slides and in open metallic slides (Fig. 30). Here again, on long exposures the rise in optical density due to the breaking down of the dye aggregates⁽⁴¹⁾ is more in glass slide mounting (Fig. 30) although on short exposures this effect is more noticeable in the case of the film exposed openly in the metal slides.

With all the evidence collected above it seems clear that temperature, and also access of moisture and air all play a part in the variations of fading rate noted between dyed films differently mounted. In more detail these effects can be

(a) Light intensity.

The light affects the film directly in the case of freely exposed films, while in the case of glass slides part of the original light is reflected back. Hence the intensity of light reaching the film is reduced.

(b) Heat.

Glass being a non-conductor of heat, it takes a longer time to heat the film sandwiched by glass slides than the one exposed open to the light source (Fig. 33). Also in the case of the freely exposed slides the metal support transmits heat very quickly to the film.

(c) Moisture and air.

It may be the absence of moisture and air which retards the fading of dyed films in glass slides. The moisture and air already present in

the film at the time it is exposed may not be sufficient to cause fading and hence the fading is more in the case of films having an air gap (Fig. 31(a),(c); 32(c)) or in an open exposure (metallic slide) where it is in a direct contact with the atmosphere.

Effect of external roughness of the
film on dye fading

The better light fastness of the dye on the gelatin film mounted on the ground glass compared with that on the unground glass is probably due to the light being scattered by the ground surface of the glass slide (Fig. 35, 2(c)), as every other factor is the same.

Different grades of Carborundum powder were used to find if the results are affected by differences in light scattering, 80^{'s} Grade is the roughest quality powder and 600^{'s} Grade is the finest. Thus the maximum light should be scattered by 600^{'s} as this will have the maximum number of grooves in a particular fixed area as compared to those of 220^{'s} and 80^{'s} in the same area. The results obtained agree with this hypothesis in that the percentage fading figures are 55, 65, and 67.3 respectively. (Fig. 2)

By grinding both surfaces of the glass slides it was found that the fading decreased still further in each case (Fig. 2). Therefore the results suggest that the lower fading rate of dyes on wool compared with gelatin may be due to light scattering effects.

It was hoped to extend this investigation by using different qualities of wool, e.g. 48^{'s}, which is a very coarse variety and Cashmere which is a very fine variety, but unfortunately it was not possible to

obtain suitable material.

Weissbein and Coven's tests correlated
with fading rate curves

The fading rate curves of all dyes were classified by Giles⁽⁴⁶⁾ into five different shapes (Fig. 1), as already mentioned (see Introduction). The fading rate curves were obtained for all the dyes (Fig. 85, 86) used in electron micrographic tests by Weissbein and Coven, in the hope that they would reveal correspondence with the electron micrographic evidence of the presence or absence of aggregates. Most of these curves can be classified as type II, wherein the dye at first fades with first order reaction, and then by a slower, zero-order, reaction, i.e., at a constant rate. This is indicative of dye being partly in molecular dispersion, and partly particulate. The dye Calcodur Violet N shows negative fading in the beginning, which has been shown (Rahman 1961, Oct.) to be caused by disintegration of dye particles in heat of illumination. Calcodur Blue 6G fading is of type III fading and indicative of particles, and Blue 4GL shows a type II fade with very small initial portion. Chlorazol Sky Blue FF, which showed no aggregated form by electron microscopy, also by its fading rate curves appears to be at least partly in molecular dispersion and partly in aggregated form. These results are clearer when the rate curve scales are expanded, but nevertheless the correspondence between electron micrography (EM) and type of fade, while satisfactory, is not as sharp as had been hoped, that is, the distinction between dyes showing or not showing aggregation by EM is not so clear cut

in the rate tests.

The y/x band ratio of different dyes
in different media

Most of the dyes show both x and y bands in their absorption spectra of visible region. The ratio between the two wavebands (i.e. y/x) increases with the increase in dye concentration in any medium⁽⁴²⁾. A "Solvo-Chromatic" shift of both the bands was observed in case of Chlorazol Sky Blue FF in Cellophane films and in water. There was no difference in the position of y and x bands in the case of normal and "gel" (undried) Cellophane films. This is probably due to the fact that both are the same chemically and differ only in their crystallinity. The results (Table 5 and Fig. 87) showed that ^{possibly} larger aggregates are formed in the gel-Cellophane. The measurements of the dye solutions before and after dyeing Cellophane and gel-Cellophane showed a higher uptake in the latter (Table 18, 18^(a)). There was no Solvo-chromatic effect between the dry and wet Cellophane and gel-Cellophane, unlike Rahman's results⁽⁴²⁾, the possible reason for this difference could be that he measured the y/x bands by keeping the wet films in water in a 1 cm. cell and here the measurements were made just of the wet film alone (taken in wet condition after dyeing and washing). In the previous case this "solvo-chromatic" effect in case of wet films could be due to water present in the cell and not the film itself.

The results of the tests with Procion Brilliant Orange M-GS Remazol Brilliant Blue R and Levafix Brilliant Blue EB have already been discussed before (see page number 86); these all show an increase in the y/x ratio.

with the increase in their depth of shade.

The effect of dye layer thickness on fading

At all stages fading was always greater in the film nearest to the lamp (I); and least fading was observed in the film farthest from the lamp (III). The film (II) was sandwiched in between (I) and (III) and faded with a rate less than (I) and greater than (III).

It was noticed that the fading rate decreased with the dye concentration, i.e. although A_1 , B_1 and C_1 were all nearest, but at equal distance from the lamp, the fading rate observed was least in B_1 which was deepest, and maximum in A_1 , which was the least deep in shade.

From the fading rate curves it seems that the dye is not completely in monodisperse state either in the case of Duranol Violet 2R (Fig. ⁸⁸⁻⁹⁰) on oriented polyester (as used by Daruwalla) or in the case of Chlorazol Sky Blue FF (Fig. ⁹¹⁻⁹⁴) on Cellophane. All the fading curves at the beginning show first order reaction, followed by zero order. This is not possible for a dye in monodisperse form, which would have always shown first order rate.

The change of first order to zero order could be due to the light energy not being sufficient to cause fading at the _____ A
inner layers, i.e., C and D although the light is _____ B
reaching them, or the light rays which may be _____ C
causing fading do not reach them as we measure the _____ D
light at the maximum absorption, or it might be due to the presence of some dye aggregate, which would fade last.

The presence of dye aggregates causing this effect could possibly

be supported by the results obtained (Table 8) where the percentage of fading has decreased with the rise in concentration; the latter being a contributing factor towards aggregation of dyes. Small dye aggregates would be expected to fade according to first order law, but with a smaller rate constant than the same dye in monodisperse form. Very large aggregates, or those which are protected by trapping between substrate molecules (Baxter et al) will show zero order fade. The presence of a range of sizes of small aggregates would be expected to reveal itself in fading as follows. Suppose two dyeings (I and II) are available of concentrations C_1 (greater) and C_2 (lesser). If both are faded together, then the rate of fading of I when its concentration has fallen to C_2 should be the same as II at the start. Actually it appears seldom to be so. A survey of the extensive series of unpublished results obtained ca. 1950 in this laboratory by N. Macaulay (Fig. 95-99) showed, by a process of drawing horizontal lines from the start of each curve to cut the next one above, that the rate at any given concentration was lower, the greater the initial concentration. This suggests the presence of small aggregates, though an alternative explanation might be that the photo-decomposition products of the dye act as a filter and reduce the intensity of the actinic light, but because of the "layer effect" just discussed which would greatly reduce the filter effect at the surfaces nearest the light, which are responsible for most of the fading, this does not seem to be a very important factor.

Fading of dyes in oriented and disoriented polyester film

It has already been shown by Giles et al.⁽²⁾ that fading is slower in oriented films than in disoriented films. Similar results were obtained by the author (Fig. 83,^{100, 101}). Also, humidity accelerated fading to a greater degree in disoriented films/^{(Fig. 83, 100-102).} The reason given by Giles et al.⁽²⁾ was that "diffusion restriction" operates, i.e. the moisture cannot readily penetrate into the compact crystalline structure of the oriented polyester film. It was found that the rate and the percentage of moisture uptake is higher in disoriented film than in oriented film (Fig. ^{103, 104}), as was to be expected. The "diffusion restriction" hypothesis was further established by the results obtained from fading of disperse dyed cellulose acetate film. This film showed better light fastness when sandwiched between two polyester films than when sandwiched between two cellulose triacetate films. In both the cases, since these films were sealed all round, the only possibility left for the moisture and air to reach the dyed triacetate film was through either polyester or triacetate films. Thus, the cause of better light fastness seems to be moisture "diffusion restriction" effect in case of oriented polyester film. (Fig. 5, 105).

It is proposed to repeat the test using an external (unsealed) film of cellulose acetate film with the polyester-sealed systems, and an external film of polyester with the acetate-sealed ones; this is to eliminate any possible u.v. light filtering effect with the polyester

films.

In case of cellulose triacetate film prepared during the present work, dye aggregates could be seen in electron micrographs of the dyed cellulose triacetate film. (Fig. 106-108).

Conclusion

The results described ^{or} have emphasised in many ways the importance of physical factors in determining light fastness of dyed fibres. Thus, exhaustive tests with reactive dyes while not giving a decisive conclusion, do appear to show that dye-fibre bonding plays no part in raising fastness, which is probably determined by the physical state of the dye. Other physical factors which have been shown to have an effect include the surface roughness of the fibre and also the exposure conditions, i.e. the temperature and accessibility of the substrate to air. ~~The crystallinity of the substrate to air.~~ The crystallinity of the substrate also plays a part and it is shown that fading is retarded when moisture diffusion to the dye is made more difficult by high crystallinity in the substrate, in polyester films.

References

1. Cumming, Giles, McEachran, J.S.D.C. 72, 373 (1956)
2. Giles and Rahman, T.R.J. 31, 1012 (1961)
3. Desai and Giles, J.S.D.C., 65, 639 (1949)
4. Filippychov, through Chem. Abstr. 54, 7152 (1960)
5. Timori, and Kitaoka, J. Chem. Soc. Japan 48, 479 (1927); Chem. Abstr. 22, 1855 (1928)
6. Gebhard, J.S.D.C. 25, 276, 304 (1909); 34, 74 (1918)
7. Gebhard, through Chem. Abstr. 15, 1517 (1911); 6, 1069 (1912); 7, 1613, 2518, 3231, 3666 (1913); 8, 3629 (1914); 9, 717 (1915).
8. A.A.T.C.C., Delaware Valley and New York sections, Am. Dyestuff Reprtr. 46, 861 (1957); cf. ibid. 45, 482 (1956).
9. Bedford, J.S.D.C., 75, 37 (1959)
10. Bowen, J.S.D.C. 65, 613 (1949)
11. Lewis et. al. J. Amer. Chem. Soc. (1941), 63, 3005; (1942), 64, 1774; (1944), 66, 2100; (1945), 67, 994, 1232.
12. Giles and McKay, T.R.J. 33, 7, (1963) p.561.
13. Hillson and Rideal, Proc. Roy. Soc. A216, 458 (1953)
14. Patterson and Pilling Trans. Far. Soc., Vol. 62, Part 7, (1966), p.1976
15. Patterson and Pilling, Nature, (1964), 201, 294
16. Eley and Parfitt, Trans. Far. Soc. (1955), 51, 1529.
17. Nelson, Opt. Soc. Am., (1961), 51, 1186.
18. Simpson, Kirby-Smith and Randolph, Nature, (1963) 199, 243.
19. Giles and Dwyer, J. Appl. Chem. (1963), Vol. 13, P.473
20. Morton and Hearle, Physical properties of Textile Fibres (Butterworth, London 1962)

21. Warwick, J.S.D.C., 75, 291 (1959)
22. Kuhn, Palette, Nr. 14, Autumn, (1963)
23. Luszcak, and Zukriegel, Melliand Textilber, 32, 868 (1951), 33, 535 (1952).
24. Kebaa and Maerov, TRJ, 31, 697 (1961)
25. Egerton et. al. J.S.D.C., 79, 49, (1963)
26. Lasarev, Ann. Physik 24, 661 (1907); Z. physik. Chem. 78, 657 (1911-12); through Chem. Abstr. 6, 3221 (1912); 10, 2433 (1916)
27. Salvin, et. al., A.D.R. 41, P297 (1952)
28. Couper, T.R.J. 21, 720 (1951)
29. A.A.T.C.C. Pacific S.W. Section, A.D.R. 43, P6 (1954)
30. Giles, J. Appl. Chem. Vol. 15 pp. 541-550 (1965)
31. Barker, Hirst, and Lambert, J.S.D.C. 43, 263 (1927)
32. Cunliffe and Lambert, J.S.D.C. 45, 306, 313 (1929); 46, 297 (1930); 47, 73 (1931); 48, 59, (1932)
33. Sommer, through Chem. Abstracts 28, 5243 (1934); Z. Anorg. Chem., 44, 61 (1931)
34. Eaton, Gordon and Giles, J.S.D.C. 68, 394 (1952)
35. Giles, J.S.D.C., 73, 127, (1957); T.R.J., 1961, 31, 141.
36. Baxter, Giles, McKee and Macaulay, J.S.D.C. 71, 218, (1955)
37. Weissbein and Coven, T.R.J. 30, 58, 62 (1960)
38. Giles, Baxter, Black, Macaulay and Rahman, T.R.J. 30, 934 (1960)
39. Baxter, Giles, and Lewington, J.S.D.C., 73, 386 (1957)
40. Campbell and Giles, J.S.D.C. 74, 164 (1958)
41. Giles, Baxter and Rahman, T.R.J., 31, 831 (1961)

References (Cont'd)

42. Giles, Rahman and Smith, J.C.S., 237, 1209-1215, (1961)
43. Solov'ev, Gen. Chem. U.S.S.R. 16, 953, 1416, (1946) through Chem. Abstr. 41, 2651, 5405, (1947)
44. Morton, J.S.D.C., 65, 597 (1949).
45. Merian, Melliand Textilchemie, 2, 45-50 (1965)
46. Giles I.I.C. Delft Conference 7th July (1964)
47. Lewis and Calvin, Chem. Rev. 25, 273 (1939)
48. Weissbein, J.S.D.C., 75, 537 (1959)
49. Stanciu-Stoian, (Revue Roumaine de chimie, 11 (April 1966) 523-527;
J.S.D.C. - Aug. ⁸² (1966) 325)
50. Lemin and Vickerstaff, Trans. Farad. Soc. 43, 491 (1944)
51. McKay, Trans. Farad. Soc. 61, 1787, 1965
52. Hillson and McKay, Trans. Farad. Soc., 61, 374 (1965)
53. Vickerstaff, The Physical Chemistry of Dyeing, (Oliver & Boyd, London),
2nd edn. (1954) Chap. 2 & 3
54. Craven and Datyner, J.S.D.C., 79, 515 (1963)
55. Giles and Hassan, J.S.D.C., 74, 846 (1958)
56. Krasovitskii and Pereyaslova, Doklady Akad. Nauk S.S.S.R.; 1954, 98, 71;
through J.S.D.C. 71, 193 (1955)
57. Giles, Montgomery and Tolia, T.R.J. 32, 99 (1962)
58. Klenle, Stearns, and Vander Meulen, J. Phys. Chem. 50, 363 (1946)
59. Zollinger - A.D.R., Aug. 16 (1965)
60. Schwen, and Schmidt, J.S.D.C., 75, 101 (1959)
61. Hedges, J.S.D.C., 43, 261 (1927), 44, 52, 341 (1928).
62. Elder and Tolia, private communications

63. Larosa, J.S.D.C., 70, 77 (1954)
64. Schaeffer, S.V.F. Fachorgan, 14, 669 (1959)
65. Wegmann, A.D.R., 51, 276 (1962)
66. Wegmann, Melliand Textilber 39, 408 (1958)
67. Gill, J.S.D.C., 71, 380 (1955)
68. Reuben and Hall, A.D.R. 51, 811 (1962)
69. Vickerstaff, Hexagon Digest 27 (1958)
70. Haller & Heckendorn U.S.P. 1,886, 480
71. Fierz-David and Matter, J.S.D.C., 53, 424, 1937.
72. Coffey, Chem. and Ind. 136, (1960)
73. Marshall and Peters, J.S.D.C., 63, 446 (1947)
74. Sumner, J.S.D.C., 76, 672-679 (1960)
Sumner + William
75. Ingamells, J.S.D.C., 73, 275 (1962)
76. Dawson et. al. J.S.D.C., 76, 210 (1960)
77. Trotman, Dyeing and Chemical Technology of Textile Fibres (Griffin, London), 3rd edn. (1964) Chap. 22.
78. Vickerstaff, J.S.D.C. 73, 237, (1957)
79. Nevell, J.S.D.C., 77, 158 (1961)
80. Schwertasek, Faserforsch und Textiltech., 11, 159 (1960) through
Mehta et. al., J.S.D.C., 78, 555 (1962)
81. Mehta, et. al. J.S.D.C., 78, 552 (1962)
82. Bohnert, J.S.D.C., 75, 581 (1959)
83. Wegmann, Textilber., 39, 1006 (1958)
ibid
84. Ulreoh, Am. Chem. Soc. 42, 81 (1961)
85. Reeves, J. Am. Chem. Soc. 71, 215 (1949)

86. Srivastava et. al., Proceedings Fifth Joint Technological Conference
held at SITRA, Coimbatore, December (1963) (Indian Patent application
No.87880)
87. Giles, pp. 137 Chem. and Ind. Jan. 22 (1966)
88. Ackermann and Dussy, Textilber. 42, 1167 (1961)
89. Gapponi, et. al. A.D.R., 50, 505 (1961)
90. Hall, Textile Recorder, 78, 929, (1960)
91. Ingamolls, J.S.D.C., 79, 65, 651 (1963)
92. Schaeffer, Tinctoria, 57, 418 (1960)
93. Osawa et. al., J.S.D.C., 80, 205 (1964)
94. Chokalin through Dyer, Nov 6 p.691 (1964)
95. Stamm and Zollinger, Helv. Chim. Acta 44, 1123 (1961)
96. Daruwalla and Kundalia original documentation not available (believed
Textil-Rund ca. 1965)
97. Merlan, Melliand Textilchemie 21, 45-50 (1965)
98. Toepffer, Melliand Textilber, 39, 1246 (1958)
99. Giles et. al. J.S.D.C., 78, 125 (1962)
100. Robinson and Mills, Proc. Roy. Soc. A.131, 578 (1931)
101. Gebhard, J.S.D.C., 25, 276 (1909)

TABLE 2.

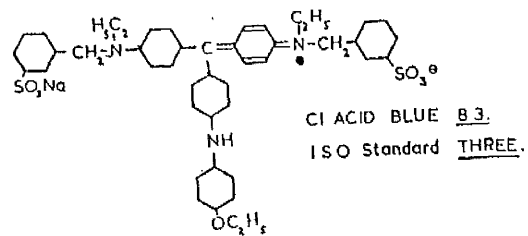
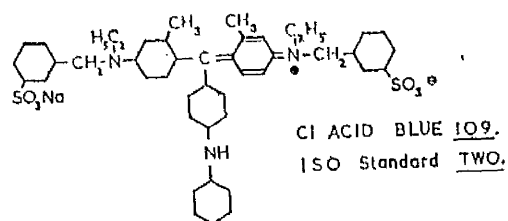
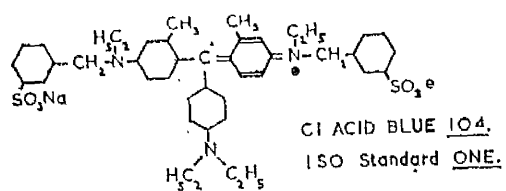


TABLE 3

Light fastness test made in a Xenotest fading in
accordance with British Standard 1006 : 1961 2-7

1.	Deepest shade on Viscose	- Unwashed	- at least 6-7
2.	" " " Mercerised Cotton	- "	- 6 duller
3.	" " " Cotton	- "	- 4-5 duller
4.	" " " Cotton	- Washed with cold water	- 5 duller
5.	" " " Mercerised Cotton	- "	- 6-7 "
6.	" " " Viscose	- "	- 5-6 "
7.	" " " Viscose	- Soaped and washed	- 6-7
8.	" " " Mercerised Cotton	- "	- 6 duller
9.	" " " Cotton	- "	- 5 duller
10.	Weakest " " Cotton	- "	- At least 6-7
11.	" " " Mercerised Cotton	- "	- At least 6-7
12.	" " " Viscose	- "	- At least 6-7

Note:

Tests were carried out by I.C.I. at their laboratory.

TABLE 4

Light fastness test made in an Atlas "Pedomotor" fading
lamp in accordance with British Standard 1006 : 1961 2-7

1.	Deepest shade in Viscose	- Unwashed	- 6-7 duller
2.	" " " Mercerised Cotton	- "	- 5-6
3.	" " " Cotton	- "	- 4-5
4.	" " " Cotton	- Washed with cold water	- 4-5 duller
5.	" " " Mercerised Cotton	- "	- 6
6.	" " " Viscose	- "	- 6 duller
7.	" " " Viscose	- Soaped and washed	- 6 duller
8.	" " " Mercerised Cotton	- "	- 5
9.	" " " Cotton	- "	- 4-5
10.	Weakest " " Cotton	- "	- At least 6-7
11.	" " " Mercerised Cotton	- "	- At least 6-7
12.	" " " Viscose	- "	- At least 6-7

Note: Tests were carried out by I.C.I. at their laboratory.

TABLE 5

Absorption spectra data (π and γ -bands) for dyes in various media.

Dye	Medium	max. band		Optical Density		O.D. ratio $\gamma:\pi$
		π	γ	π	γ	
(1)	Cellophane dry	6100	6580	0.23	0.33	0.848
		6100	6580	0.23	0.27	0.852
		6100	6580	0.51	0.60	0.850
		6100	6600	1.45	1.74	0.833
		6100	6600	1.35	1.65	0.818
		6100	6600	0.19	0.24	0.801
		6100	6600	0.36	0.46	0.777
		6100	6600	0.76	0.98	0.780
	Cellophane wet	6100	6580	0.27	0.34	0.794
		6200	6600	0.19	0.23	0.826
		6100	6580	0.48	0.61	0.790
	gel-Cellophane dry	6100	6580	1.04	1.22	0.852
		6100	6580	0.70	0.82	0.853
		6100	6580	0.92	1.08	0.852
		6100	6600	0.59	0.69	0.851
		6100	6600	3.56	4.10	0.868
		6100	6600	3.92	4.46	0.878
		6100	6600	3.68	4.20	0.876
		6100	6600	3.80	4.40	0.863
		6100	6600	0.69	0.85	0.800
		6100	6600	0.57	0.71	0.800
		6100	6600	3.36	3.90	0.861
		6100	6600	3.04	3.50	0.869
	gel-Cellophane wet	6060	6600	0.56 *	0.66 *	0.848
		6100	6580	0.34 *	0.41 *	0.830
		6100	6580	0.44 *	0.54 *	0.814
		6000	6200	0.785 *	0.91 *	0.862

Note: - Figures marked * are to be doubled.

TABLE 5 (Cont'd)

Dye	Medium	max. band		Optical Density		C.D. ratio
		λ	μ	λ	μ	$\lambda:\mu$
(2)	gel-Cellophane wet	5150	5400	0.52	0.50	1.040
	gel-Cellophane dry	5150	5400	1.08	0.96	1.120
	Cellophane wet	5150	5400	1.37	1.28	1.070
	Cellophane dry	5150	5400	0.87	0.78	1.110
(3)	gel-Cellophane wet	5900	6320	0.50	0.50	1.000
	gel-Cellophane dry	5900	6340	0.46	0.45	1.020
	Cellophane wet	5880	6340	0.32	0.34	0.940
		5900	6320	0.56	0.57	0.980
	Cellophane dry	5900	6300	0.38	0.39	0.970
		5900	6300	0.57	0.58	0.980
(1)	Deionised water	5900	6200	0.53	0.63	0.848
		5900	6200	0.27	0.32	0.844
		5900	6200	0.11	0.14	0.786
		5900	6200	0.69	0.82	0.841
		5900	6200	1.30	1.47	0.884
		5900	6200	1.88	2.07	0.911
		5900	6200	2.37	2.43	0.975
		5900	6200	0.47	0.57	0.825
		5900	6200	0.76	0.91	0.835

(1) Chlorazol Sky Blue FF (C.I. 24410)

(2) Benzopurpurin 4B (43:100) (C.I. 23500)

(3) Chlorazol Azurine G (C.I. 24140)

TABLE 6

Light fastness of reactive dyes

		<u>Fastness grading</u>	
		<u>Unfixed</u>	<u>Fixed</u>
1.	Procion Blue 3G	6	7
2.	Procion Brilliant Yellow 6G	4	7
3.	Procion Yellow H5G	3-4	6-7
4.	Procion Brilliant Orange G	4-5	6
5.	Procion Brilliant Red G	3	4-5
6.	Procion Scarlet HE	3	4
7.	Procion Blue R	5	6
8.	Procion Brilliant Red 5B	2-3	4-5

Footnote: Taken from Ingamells' paper.

TABLE 7

Light fastness of Remazol dyestuffs dyed on
mercerised cotton 1:1 depth

	<u>Unfixed</u>	<u>Fixed</u>
Remazol Yellow G	4-5	6
" Brilliant Orange 3R	4	5-6
" Brilliant Red BB	4	5
" Brilliant Violet SR	6-7	6-7
" Blue 3R	6-7	6-7
" Brilliant Blue R	6-7	6-7
" Turquoise Blue G	6-7	6-7
" Brilliant Green 6B	6-7	6-7
" Grey G	6-7	6
" Black B	6	5-6

Note: Data supplied by manufacturers.

TABLE 8

Fading of Cibacron Scarlet 2G on Cellophane

	<u>Initial</u>	<u>After Fading</u> <u>230 hr.</u>	<u>Fading</u>
	O.D.	O.D.	(%)
Unfixed	1.67	1.46	12.5
Fixed	.612	0.506	17.3
Methanol Treated	0.94	0.80	14.9

TABLE 9

Spectral data of dyes

<u>Dye</u>	<u>Medium</u>	<u>max. band</u>		<u>O.D. at max. (x) in 1 cm. cell conc(g)</u>	<u>O.D. ratio y:x</u>
		<u>y</u>	<u>x</u>		
(1)	Water	4950	5250	0.125	0.76
	Water	"	"	0.498	0.80
	Water	"	"	0.995	0.83
	Water	"	"	1.990	0.86
	Cellulose (after alkali treatment)	5050	5500	0.111	0.91
		"	"	0.545	1.01
		"	"	1.300	1.08
(2)	Water	5000	(5200?)	0.172	1.10
	Water	"	"	0.585	1.14
	Water	"	"	1.760	1.14
	Cellulose (after alkali treatment)	5100	5350	0.068	1.02
		"	"	0.73	1.12
		"	"	1.46	1.12
(3)	Water	6200	6600	0.074	0.43
	Water	"	"	0.382	0.68
	Water	"	"	1.340	0.81
	Cellulose	6250	6630	0.494	0.65
	Cellulose	"	"	1.460	0.66

Note: Taken from Rehman's thesis.

(1) Cibacron Rubine R (Ciba)

(2) Cibacron Scarlet 2G (Ciba)

(3) Procion Brilliant Blue 7BG (I.C.I.)

Footnote: Wavelengths are given in parenthesis where the peak is flat or in the form of a shoulder; a query indicates very indefinite peak.

TABLE 10

Light fastness of reactive dyes

	<u>Cotton</u>	<u>Depth</u> ^{**}	<u>Viscose rayon</u>
Levafix Brilliant Blue E.R.	6	1	6-7
	6	2	6-7
	5-6	3	6-7
	5-6	4	6-7
<hr/>			
Levafix Brilliant Blue E.B.	6	1	6
	6	2	6
	5-6	3	6
	5	4	6

- ^{**} 1 = $\frac{1}{12}$ of the standard depth
 2 = $\frac{1}{6}$ of the standard depth
 3 = $\frac{1}{3}$ of the standard depth
 4 = The standard depth

Figures taken from shade cards ($\frac{1e897e}{F_{2.}}$) and ($\frac{1e1017e}{F_{2.}}$)

TABLE II

Light fastness tests of Iovafix Brilliant Blue E.B.on poplin dyed by thermosol process

Tests carried out at -	1		2		3		4		5		6		7		8		9	
	15g/l.		30g/l.		45g/l.		45g/l.		45g/l.		45g/l.		15g/l.		15g/l.		30g/l.	
	Fixed Soaped	Fixed Soaped	Fixed Soaped	Fixed Soaped	Fixed Soaped	Fixed Soaped	Unfixed Washed Cold	Unfixed Washed Cold	Unfixed Not washed	Unfixed Washed Cold	Unfixed Washed Cold	Unfixed Washed Cold	Unfixed Not washed	Unfixed Washed Cold	Unfixed Washed Cold	Unfixed Washed Cold	Unfixed Washed Cold	Unfixed Washed Cold

Half
Urea &
Half Soda
Carbonate
Soaped

Templeton

5

Faded
earliest
and max.

4

4

4

5

Better than
1, 2, 3

4-5

4

4-5

5

Bayer 71 hrs.
(Xenotest)

4

3-4

3-4

5

5-6

5

3-4

4

4

Note: There was no fading beyond standard 6 and very little in case of 5

This laboratory
189 hrs.Faded
less
than 2
& 3 the
other
two
fixed
dyeings.Both faded
equallyFaded
littleFaded very
little less
than 4

Faded

All faded more than 1, 2 & 3.

TABLE 12

Light fastness tests of Levafix Brilliant Yellow E-22on rayon dyed by thermosol process.

	1	2	3	4	5	6	7	8	9
Tests carried out at -	15g/l.	15g/l.	15g/l.	30g/l.	30g/l.	45g/l.	45g/l.	45g/l.	30g/l.
	Fixed	Unfixed	Unfixed	Fixed	Unfixed	Fixed	Unfixed	Unfixed	Fixed Half Urea
	Scoured	Unwashed	Washed Gold	Scoured	Washed Gold	Scoured	Unwashed	Washed Gold	Sodium Carbonate
									Scoured

Temploton

4-5

5-6

5

4-5

5

5

3-4

5-6

Bayer
71 hr.

6

3

4-5

6

5-6

6

4

5-6

Note: There was no fading beyond standard 6 and very little in case of 5.

This laboratory
189 hr.Very faded and faded less
little quite than 2
fading wellFaded
better
than 2Practi-
cally no
fadingBetter
than 7Not
very
goodQuite
goodBetter than 6
(same as 4)

TABLE 13

Light fastness tests of Levafix Brilliant Red E-1B. (30g/l)on poplin by thermo fixation process

<u>Tests carried out at</u>	<u>Normal fixed dyeing</u>	<u>Half Urea & Sodium Carbonate</u>	<u>No Urea and Sodium Carbonate Unfixed, Washed cold</u>
Bayer for 71 hr. (Kenotest)	4-5	4-5	4-5

Note: There was no fading beyond standard 6 and very little in case of 5.

Templeton	4-5	4-5	5
-----------	-----	-----	---

This laboratory 189 hr. All faded more or less the same.

TABLE 14

L.F. results as supplied by BASF, U.K.

(1) dried at 60°C.	3	}	Primazine Brill. Orange R 40g./l
(2) steamed 1 min. at 100°C	3-4		
(3) steamed, rinsed	4		
(4) steamed, rinsed, soaped	4-5		
(1) dried at 60°C.	3-4	}	Primazine Scarlet R 40g/l.
(2) steamed 1 min. at 100°C	3		
(3) steamed, rinsed	4		
(4) steamed, rinsed, soaped	4		
(1) dried at 60°C.	3	}	Primazine Brill. Pink B.
(2) steamed 1 min. at 100°C	3-4		
(3) steamed, rinsed	5		
(4) steamed, rinsed soap	4-5		
(1) dried at 60°C	3	}	Primazine Red P-3B 40g/l.
(2) steamed 1 min. at 100°C	3-4		
(3) steamed, rinsed	5		
(4) steamed, rinsed, soaped	4-5		

Sample exposed in Fadeometer against Blue Standard for 230 hrs.

Note:

Rinsed and steamed patterns much weaker in all cases. Suggests: loose surface colour is not fast.

TABLE 15

Density measurements of the fixed and the
unfixed dyed Cellonhane films

		<u>Density</u>
Undyed		1.523g/c.c.
Fixed dyed	} Procion Brilliant Red M-5 BS	1.525g/c.c.
Fixed dyed		1.525g/c.c.
Unfixed dyed		1.525g/c.c.
Unfixed dyed		1.522g/c.c.
Fixed dyed	} Procion Brilliant Yellow 6 BS	1.524g/c.c.
Fixed dyed		1.522g/c.c.
Unfixed dyed		1.525g/c.c.
Unfixed dyed		1.525g/c.c.

a Footnote:

The measurements were made by Mr. Tripathi (in the Fibre Science Department of this University) using a density gradient column, ^{of} Carbon tetrachloride and Xylene. The column was calibrated by using glass beads of known density. The density results were obtained with an accuracy of ± 0.0005 .

TABLE 16

Light fastness of Levafix Brilliant Blue E.B.

<u>Unfixed and unwashed</u>				<u>Fixed and soaped</u>		
<u>Viscose</u>	<u>Mercerised Cotton</u>	<u>Cotton</u>	<u>Depth of Shade</u>	<u>Cotton</u>	<u>Mercerised Cotton</u>	<u>Viscose</u>
			$1/12$	6-7	7	7-8
6-7	5-6	5	$1/6$	6	6	7
6-7	6	5	$1/3$	5-6	5-6	6
7-8	6-7	6	$1/1$	5	5-6	6

Note:

Tests carried out at J. & P. Coats Ltd.

TABLE 17

Effect of substituents on the light fastness of dyes

<u>Dye</u>	<u>L.F.</u>	<u>Group attached</u>	<u>Dye</u>	<u>L.F.</u>
C.I. 11210	5	OH	C.I. 11225	4-5
C.I. 60505	7	OH	C.I. 60715	5
C.I. 11130	4-5	Cl	C.I. 11150	5-6
C.I. 11110	5	Cl	C.I. 11115	6
C.I. 11210	5	Cl	C.I. 11215	6
C.I. 11025	4-5	Cl	C.I. 11035	5
C.I. 60505	7	NHCH ₃	C.I. 61500	5

L.F. = Light fastness.

Each dye in Column 4 has the same structure as the corresponding in Column 1, but with the group attached shown.

TABLE 18

Dye Concentration of Solutions (in terms of O.D.)

<u>Original</u>	<u>After dyeing</u>	
	<u>gel-Cellophane</u>	<u>Cellophane</u>
0.38 (10^3)	0.315	0.355
0.38 (10^3)	0.315	0.360
0.38 (10^3)	0.310	0.338

TABLE 18 (a)

Concentrations of dye solutions (in terms of O.D.)

<u>Before dyeing</u>	<u>After dyeing</u> <u>gel-Cellophane</u>	<u>after dyeing</u> <u>Cellophane</u>
0.321	0.205	0.316
0.93	0.606	0.86
0.195 (10^3)	0.133 (10^3)	0.157 (10^3 all)

Note: All solutions were diluted to 10 times.

x These were further diluted to 10 times.

TABLE 19

Light Fastness & Wash Fastness dataShade depths = $\frac{1}{25}$, $\frac{1}{12}$, $\frac{1}{6}$, $\frac{1}{3}$, $\frac{1}{1}$

<u>Dyes</u>	<u>L.F.</u>		<u>W.F.</u>	
	<u>Cotton</u>	<u>Raven</u>	<u>Cotton</u>	<u>Raven</u>
Primazin Yellow G.L.	3-4 4 4-5 5 6	3-4 4 4-5 5 6	4 5 5 5 5	4 5 5 5 5
Primazin Brill. Orange R	3-4 4 5 5 5-6	3-4 4 5 5 5-6	4-5 4-5 4-5 4-5 4-5	4-5 4-5 4-5 4-5 4-5
Primazine Scarlet R	3 3-4 4 4-5 5	3 3-4 4 4-5 5	4-5 5 5 5 5	4-5 5 5 5 5
Primazin Red P-3B	3 3-4 4 4 4-5	3 3-4 4-5 4-5 5	4 5 5 5 5	4 5 5 5 4-5
Primazin Brill. Pink B.	3 3 4 4-5 5	3 3 4 4-5 5	4-5 5 5 5 5	4-5 5 5 5 5
Primazin Grey P-BL	3-4 4 4-5 4-5 6	4 4-5 5 5 6	4-5 5 5 5 5	4 4-5 4-5 4-5 4-5

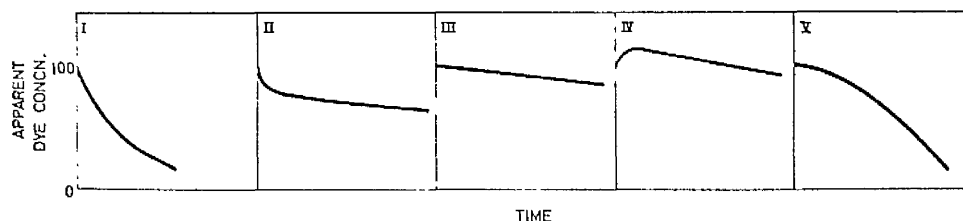


Fig. 4 *Diagram of types of fading-rate curves of colorants*

- I. First- or second-order fading. Dye probably in molecular dispersion. Rarely occurs.
- II. Initially as I, followed by a slow fading at constant rate (zero order). Dye probably partly in molecular dispersion, partly particulate. Occurs most often.
- III. Entirely constant rate of fading. Dye probably entirely particulate. Occurs often with pigments and fast dyes.
- IV. Negative initial fading, caused by disintegration of dye particles in heat of illumination. Occurs with some fast dyes.
- V. Fading which accelerates with time. Caused by continued breakdown of dye particles. Obtained with some insoluble azo dyes in cellulose.

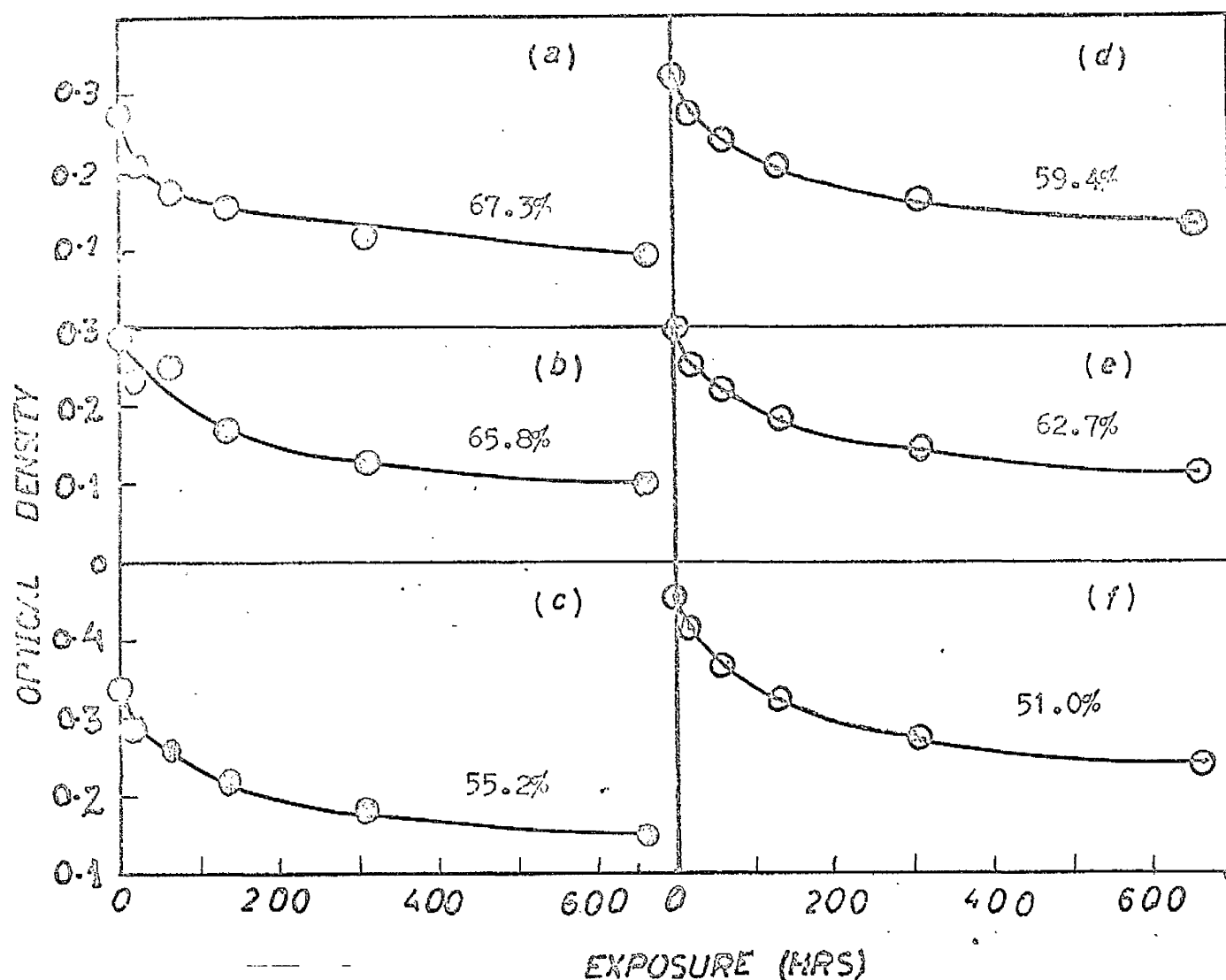


Fig. 2 Fading of p-Nitroaniline-R-acid (Na salt) on gelatine film mounted on ground glass.

(a), (b) & (c) : Ground on one side only.

(d), (e) & (f) : Ground on both sides.

(a) & (d) : Carborundum powder grade 80.

(b) & (e) : Carborundum powder grade 220.

(c) & (f) : Carborundum powder grade 600.

Percentage fading is shown on each curve.

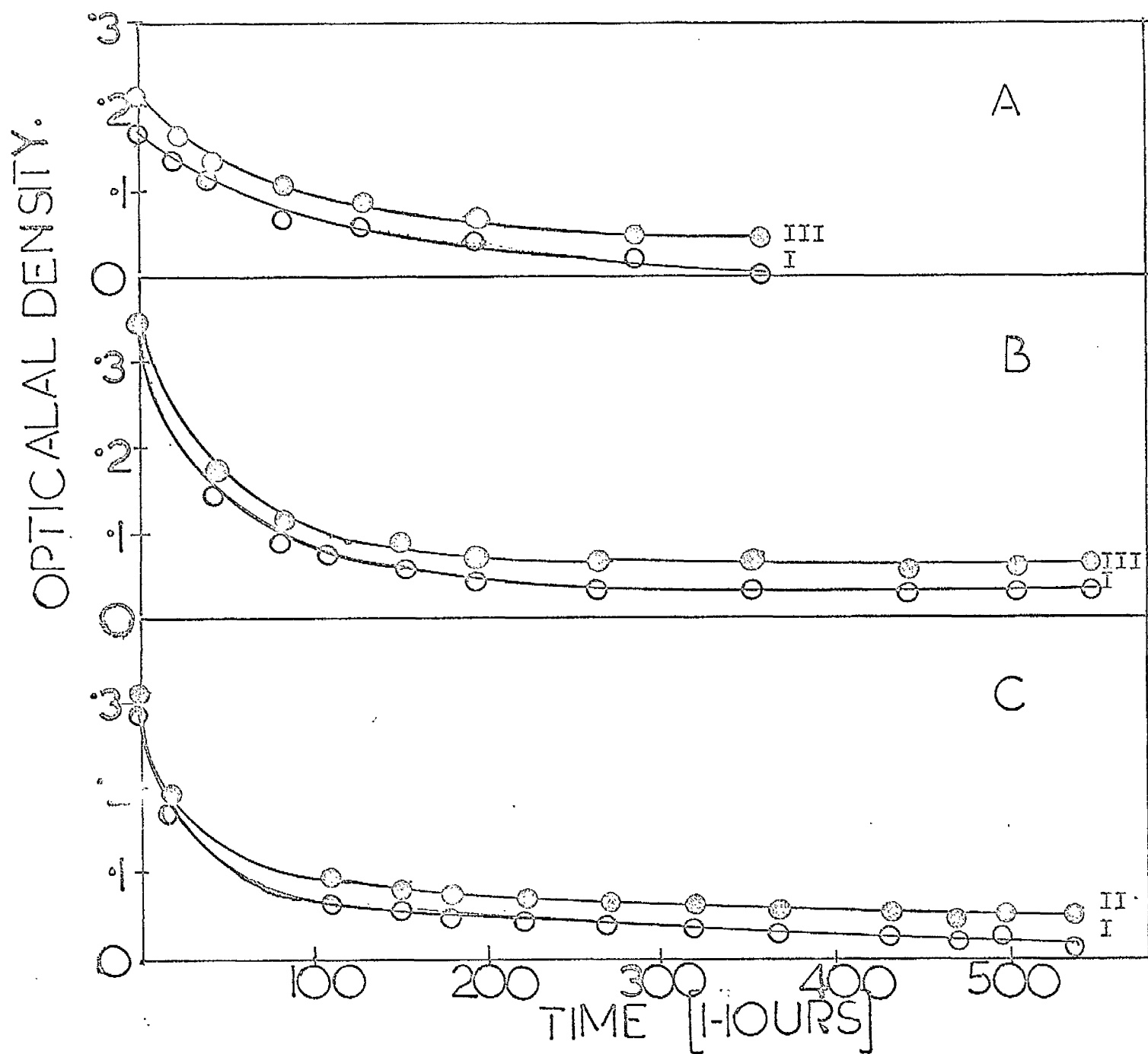


Fig. 2(a) Fading of acid dyes on gelatine film mounted on plane and ground glass.

(a) p-nitroaniline \rightarrow R-acid (Na salt).

(b) & (c) Acid Magenta A150

I : Plane glass.

II : Ground on one side (Carborundum powder grade 80).

III : Ground on both sides (Carborundum powder grade 120).

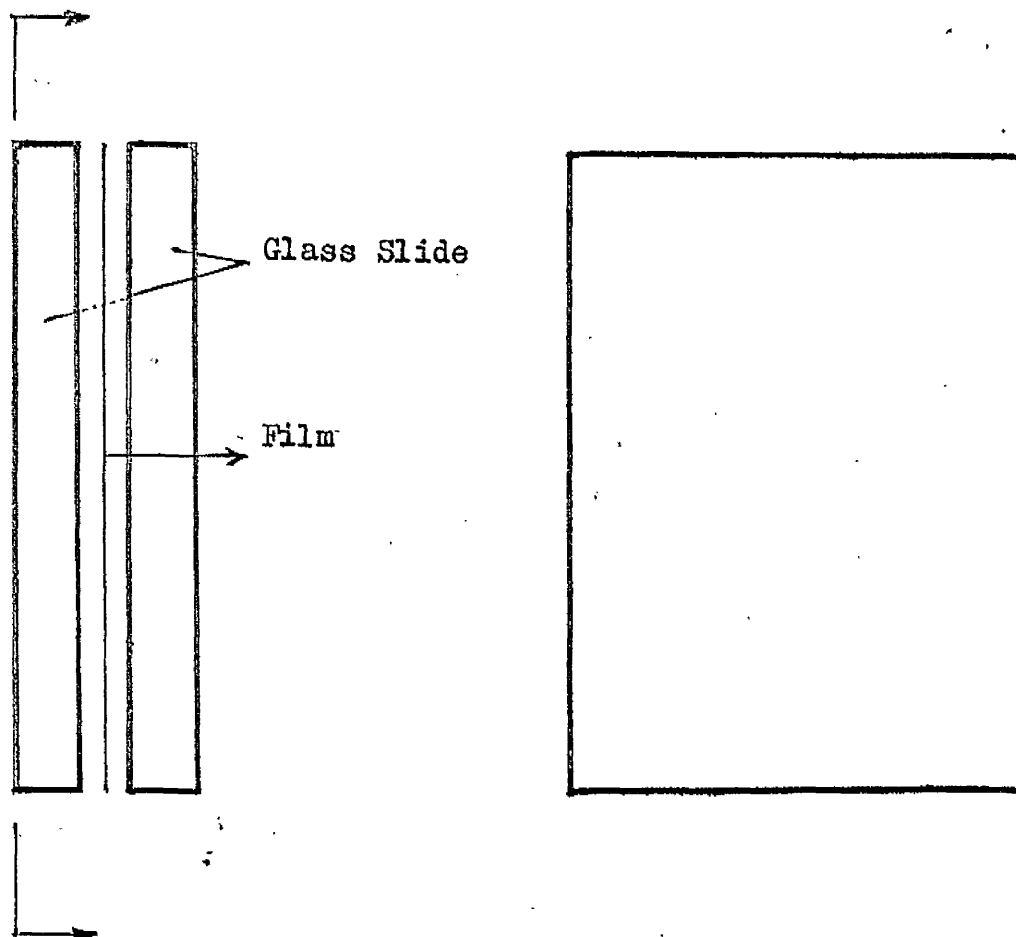
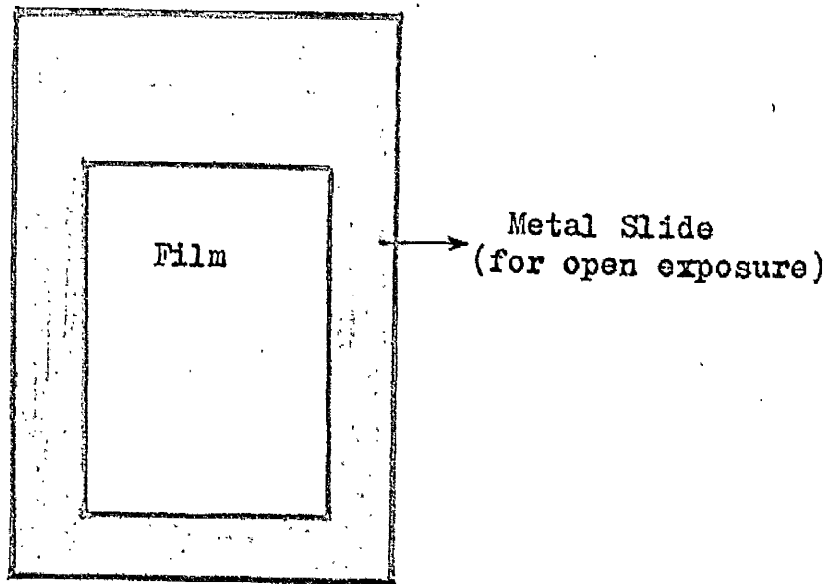


Fig. 3

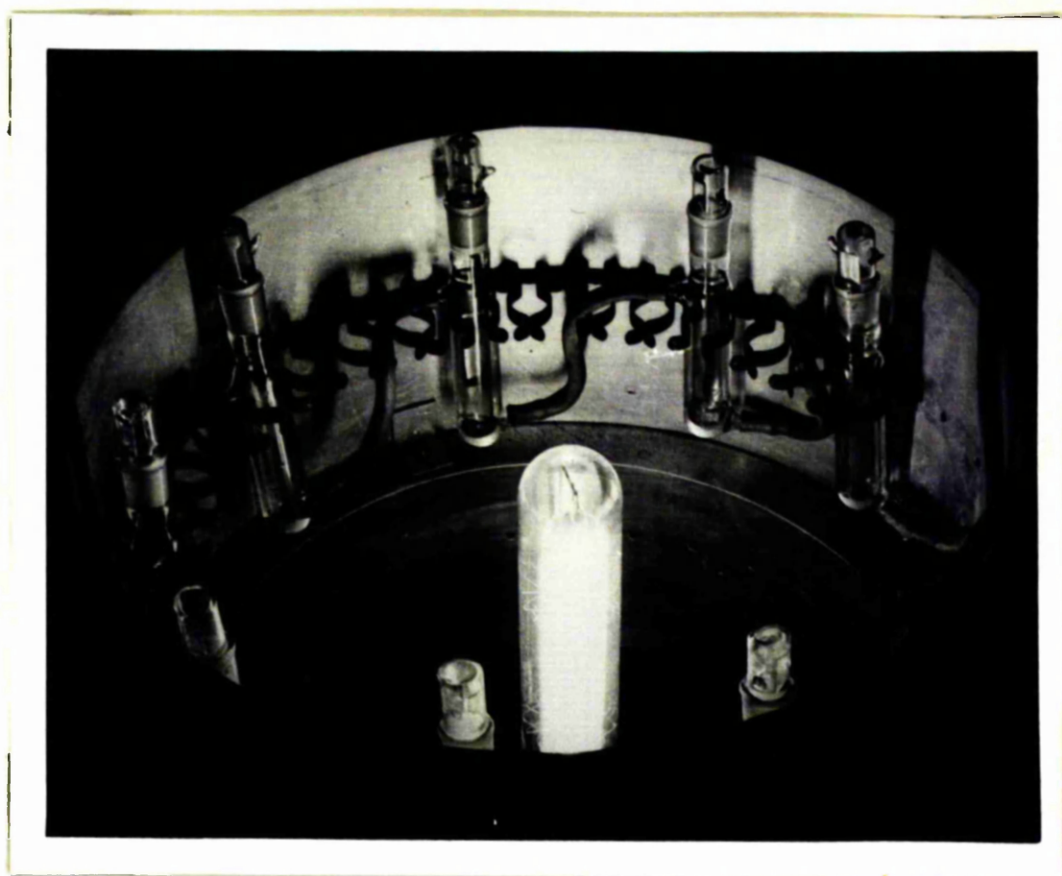


Fig. 4

A general view of the fading lamp used as a source
of irradiation during investigations.

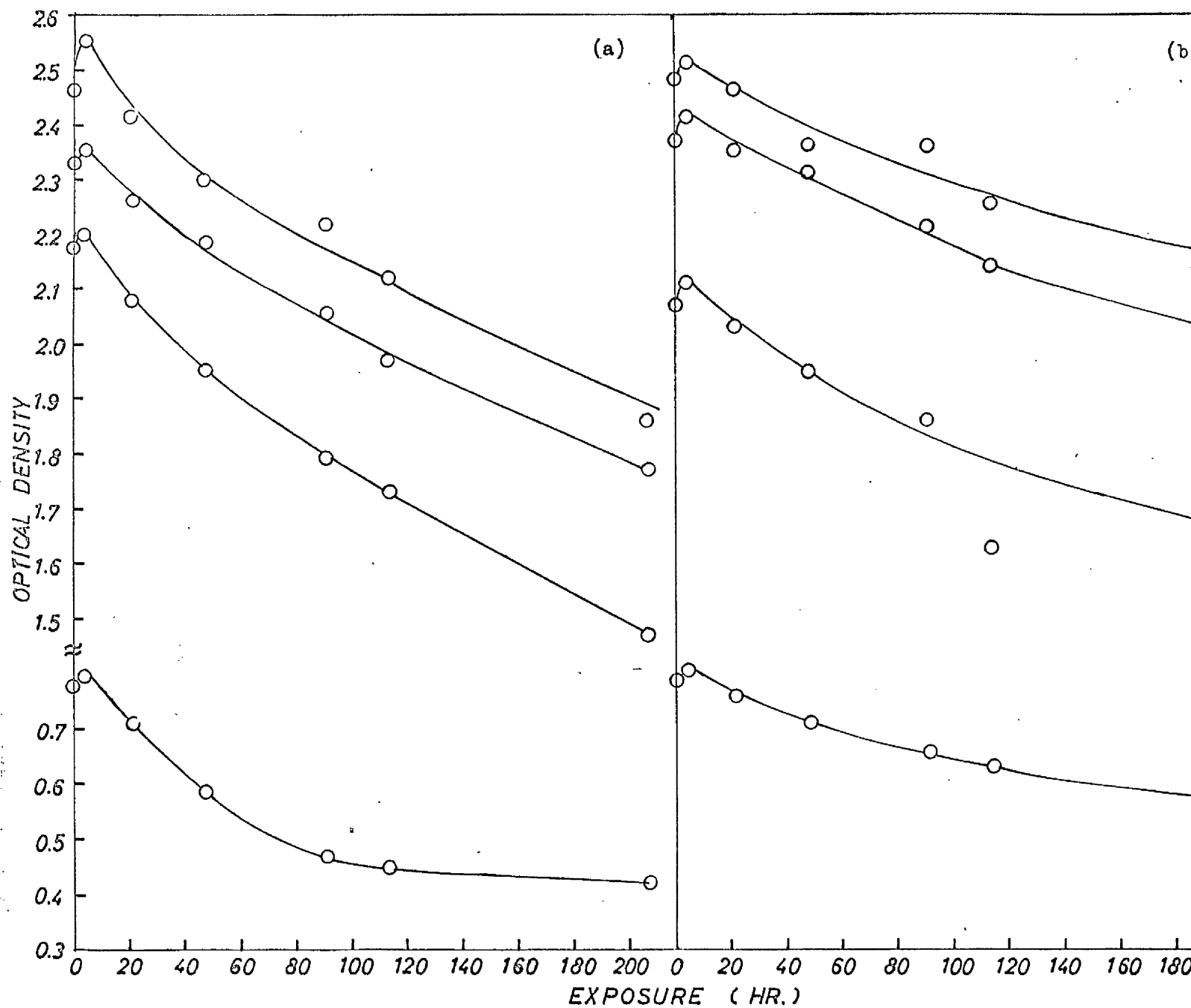


Fig. 5 Fading of Dispersol Fast Orange A 150 Pdr. on Cellulose triacetate sandwiched between (a) Cellulose triacetate films, and (b) Polyester films.

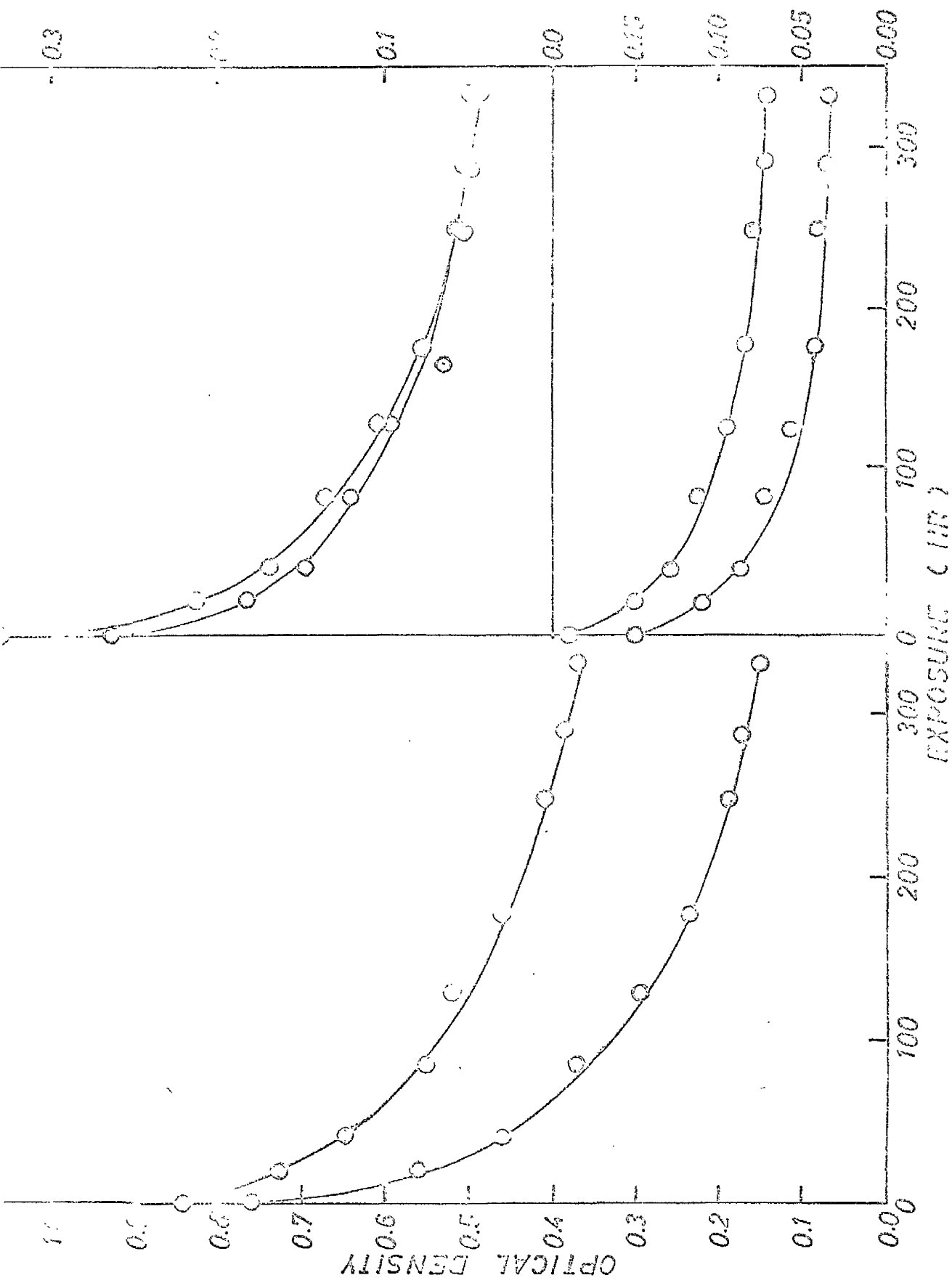


Fig. 6 Fading of the G-25 dye in the presence of glucose and pyruvate.

○ Type 1 Glucose.

○ Type 2.

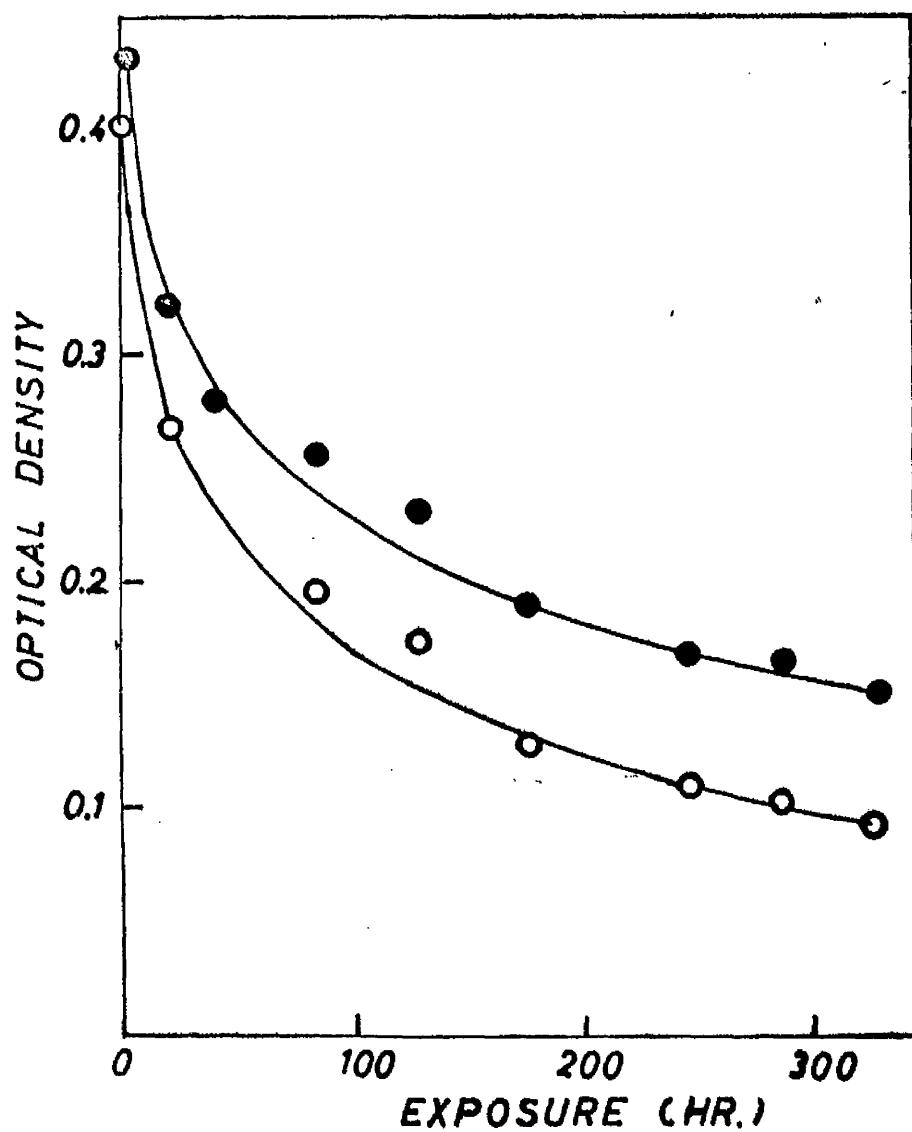


Fig. 7 Fading of the Cellofas film dyed with Procion Brilliant Red M - 5BS.

- Dye + Glucose.
- Dye.

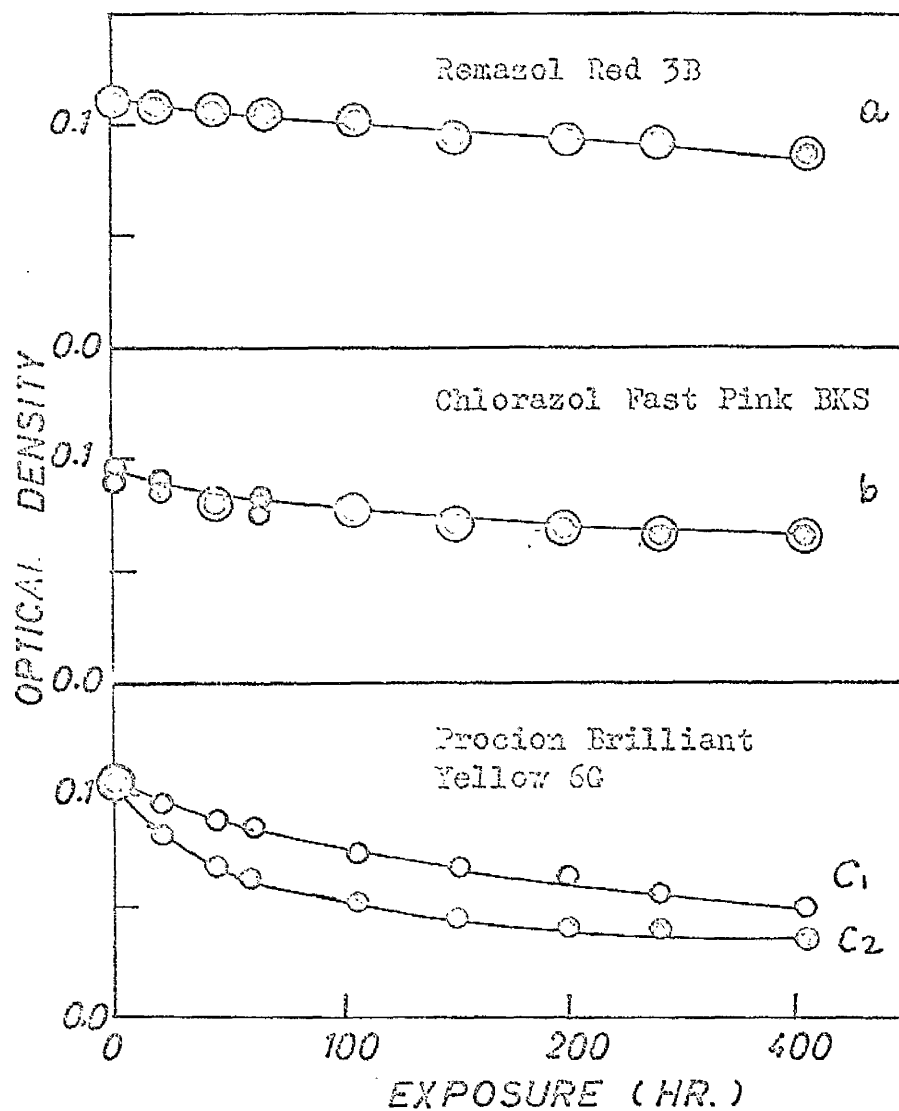


Fig. 8 Fading of dyed Cellofas films with glucose at pH 10.5 (\odot) and at pH 5.0 (\circ).

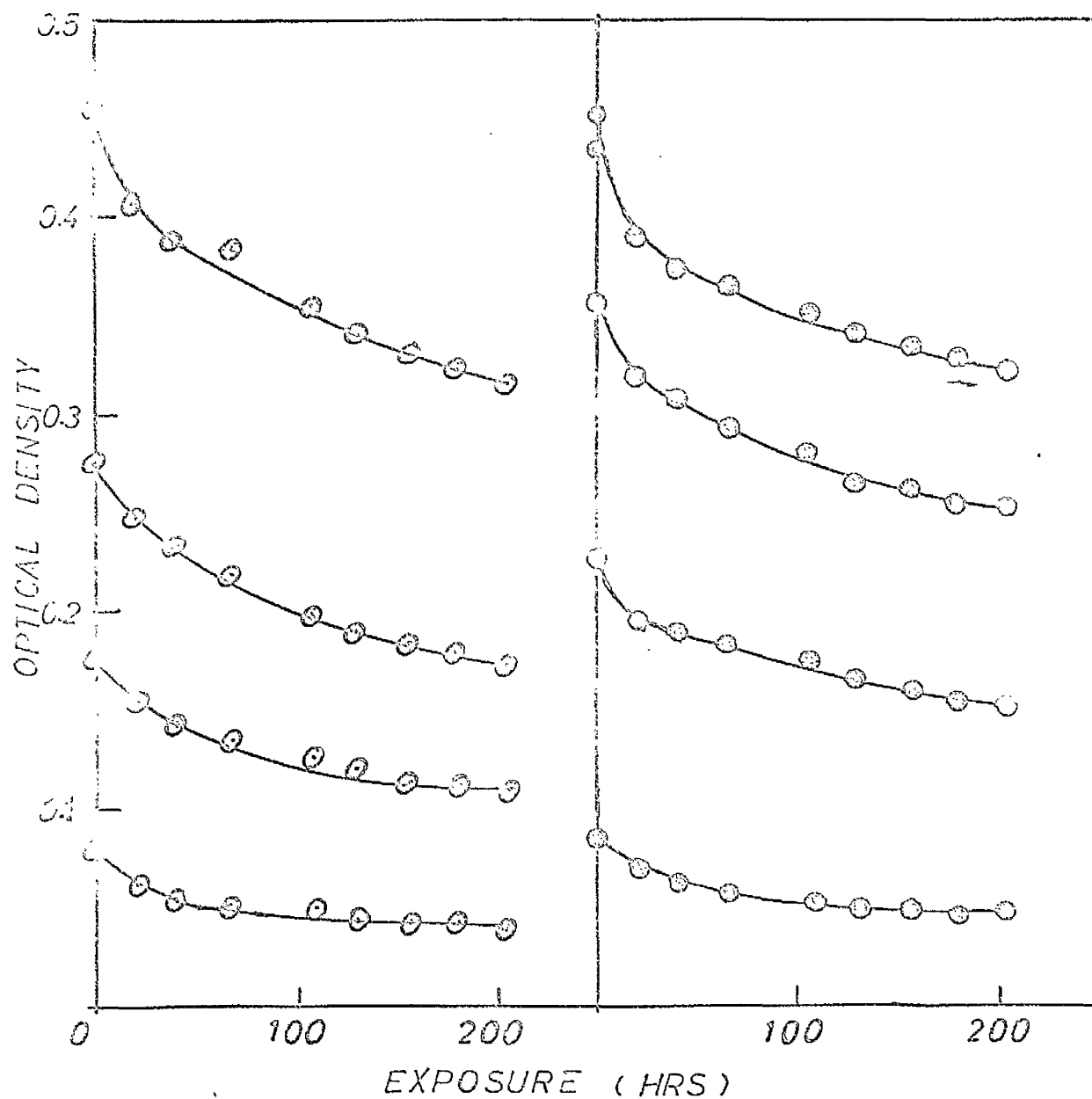


Fig. 9 Fading of Cellofas films dyed with Precion Brilliant Orange G with glucose at pH 10.5 (O) and pH 5.0 (●).

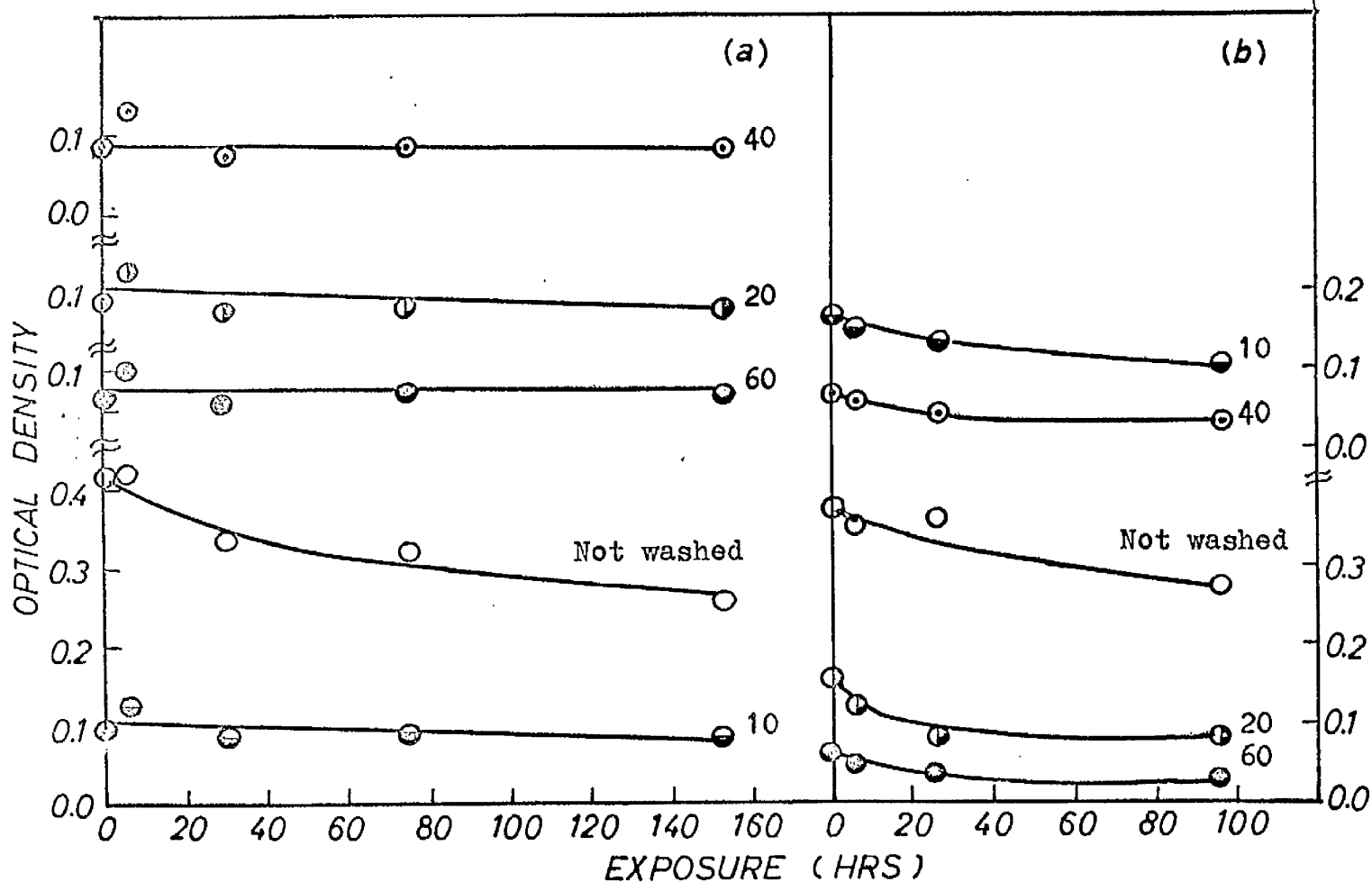


Fig.10 Fading of (a) Procion Brilliant Yellow 6G, and (b) Procion Brilliant Orange MGS, after different washing times. Washing times are indicated in minutes beside each curve.

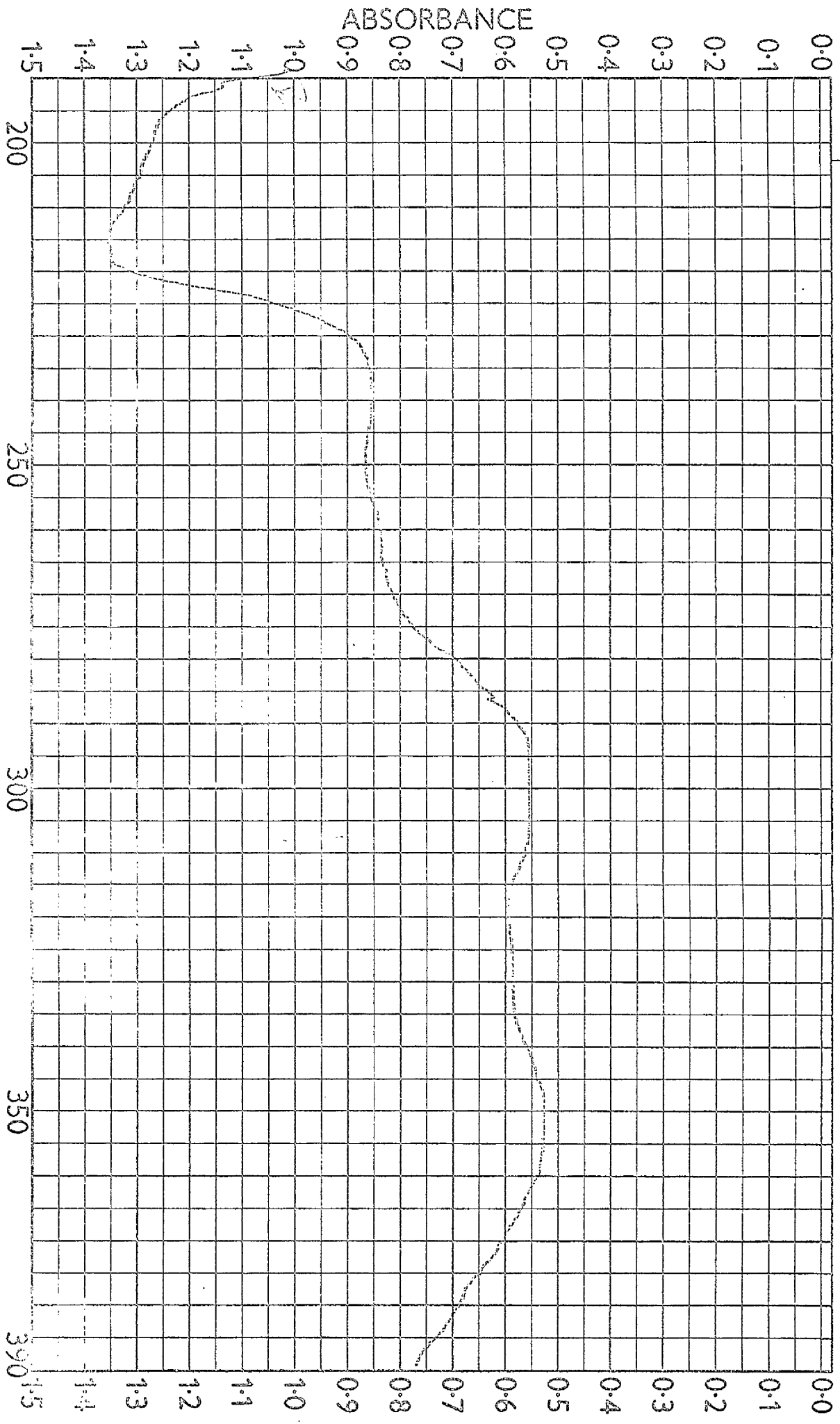


Fig. 11 Lead curve after irradiation.

SAMPLE <u>Dye A</u> ORIGIN _____ SOLVENT <u>Triethylamine</u>	CURVE NO. _____ CONC _____ CELL PATH <u>1 mm</u> REFERENCE _____
SCAN SPEED <u>1000</u> SLIT <u>25</u>	
OPERATOR <u>W</u> DATE <u>10/16/66</u>	
REMARKS _____	

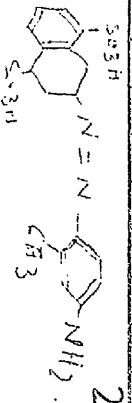
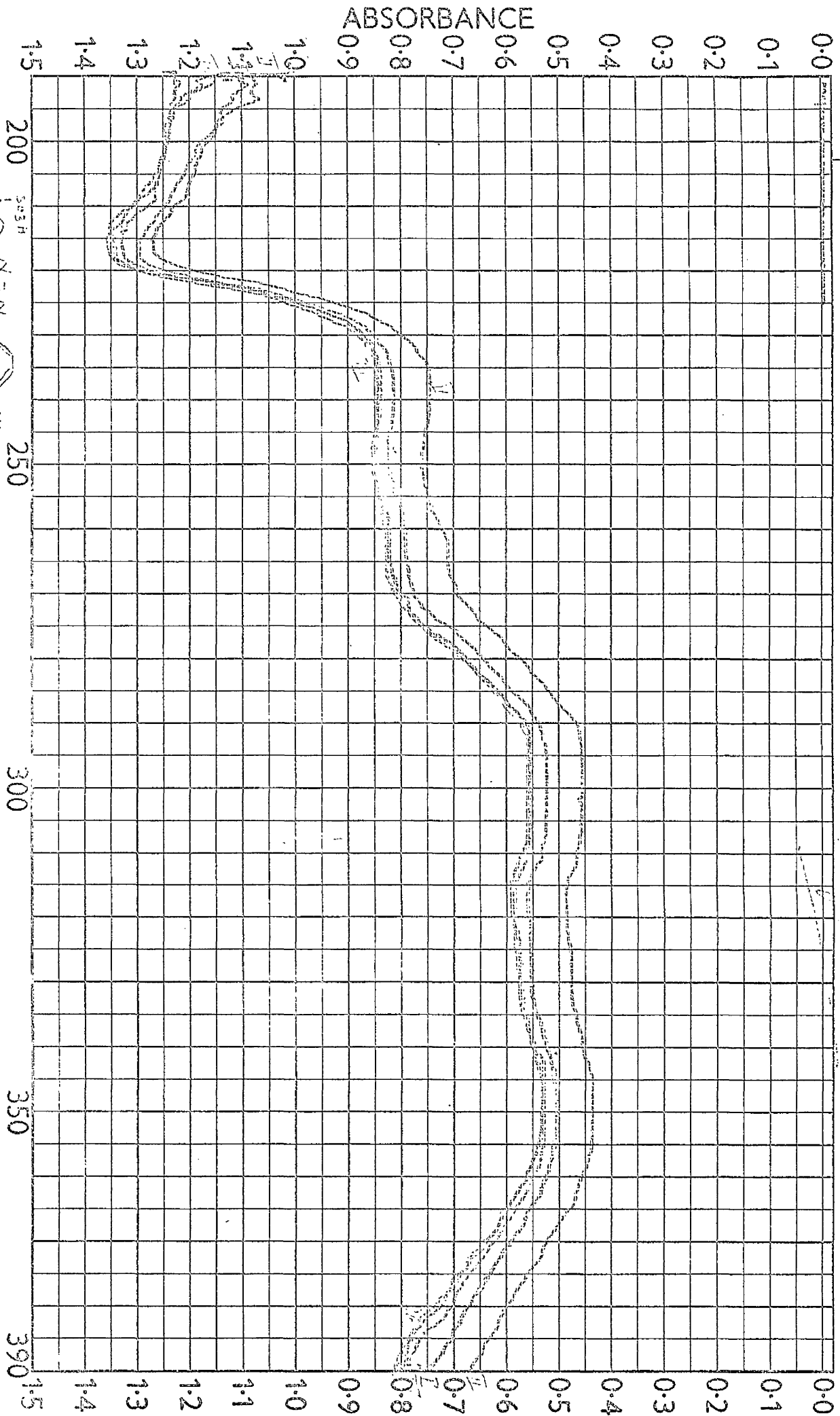


Fig. 11(a)

SAMPLE <u>Indole H.</u>	CURVE NO. <u>1</u>	SCAN SPEED <u>100</u>	OPERATOR <u>P. J.</u>
ORIGIN <u>Ind. Lab.</u>	CONC <u>1 mg/ml</u>	SLIT <u>2 mm</u>	DATE <u>10/14/66</u>
SOLVENT <u>Ind. Lab.</u>	CELL PATH <u>1 cm</u>	REFERENCE <u>Blank</u>	REMARKS <u></u>

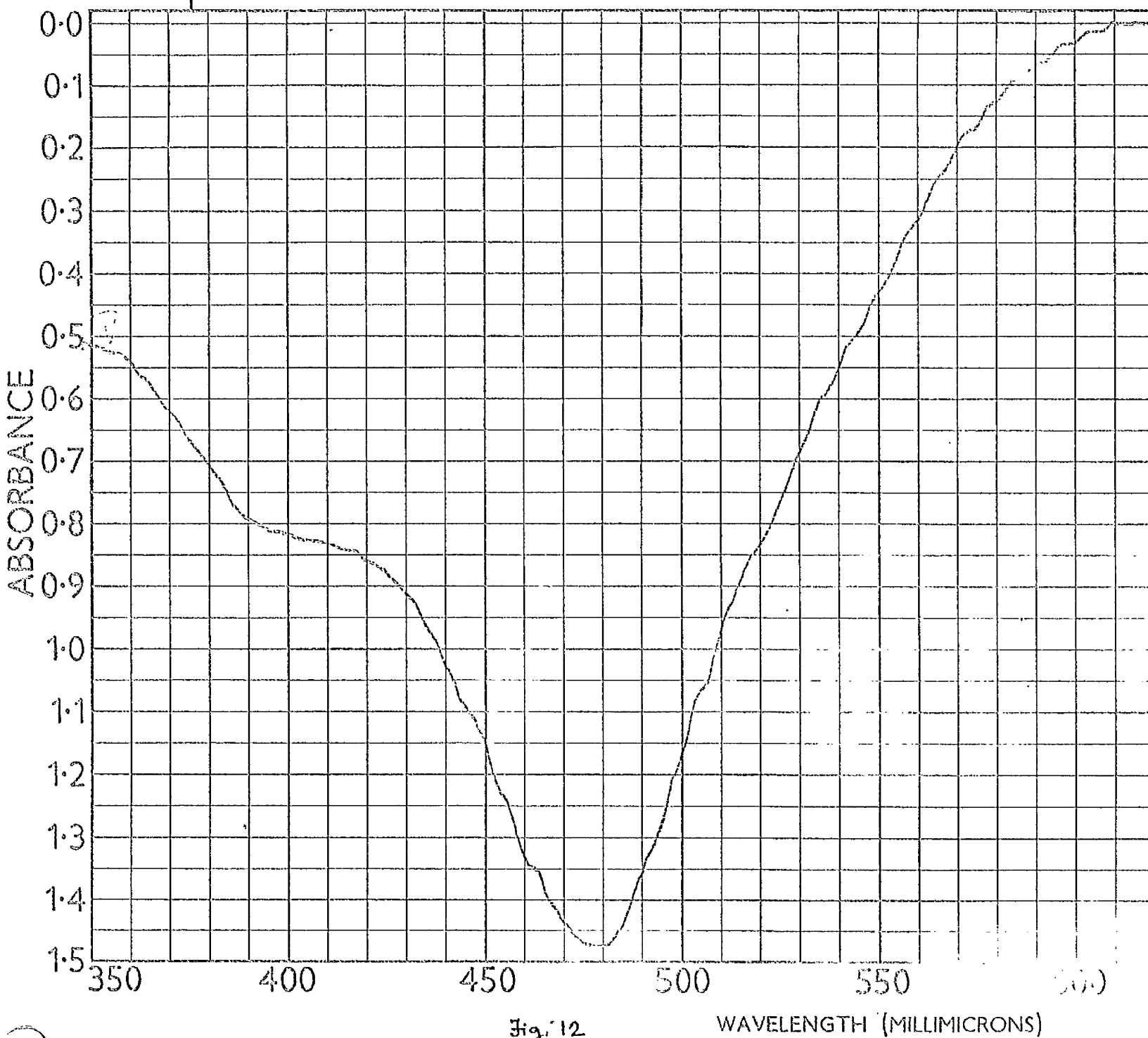


Fig. 12
Last curve after irradiation

SAMPLE <u>Type A</u>	CURVE NO _____
ORIGIN _____	CONC _____
SOLVENT <u>Toluene</u>	CELL PATH <u>1 cm</u>
	REFERENCE _____

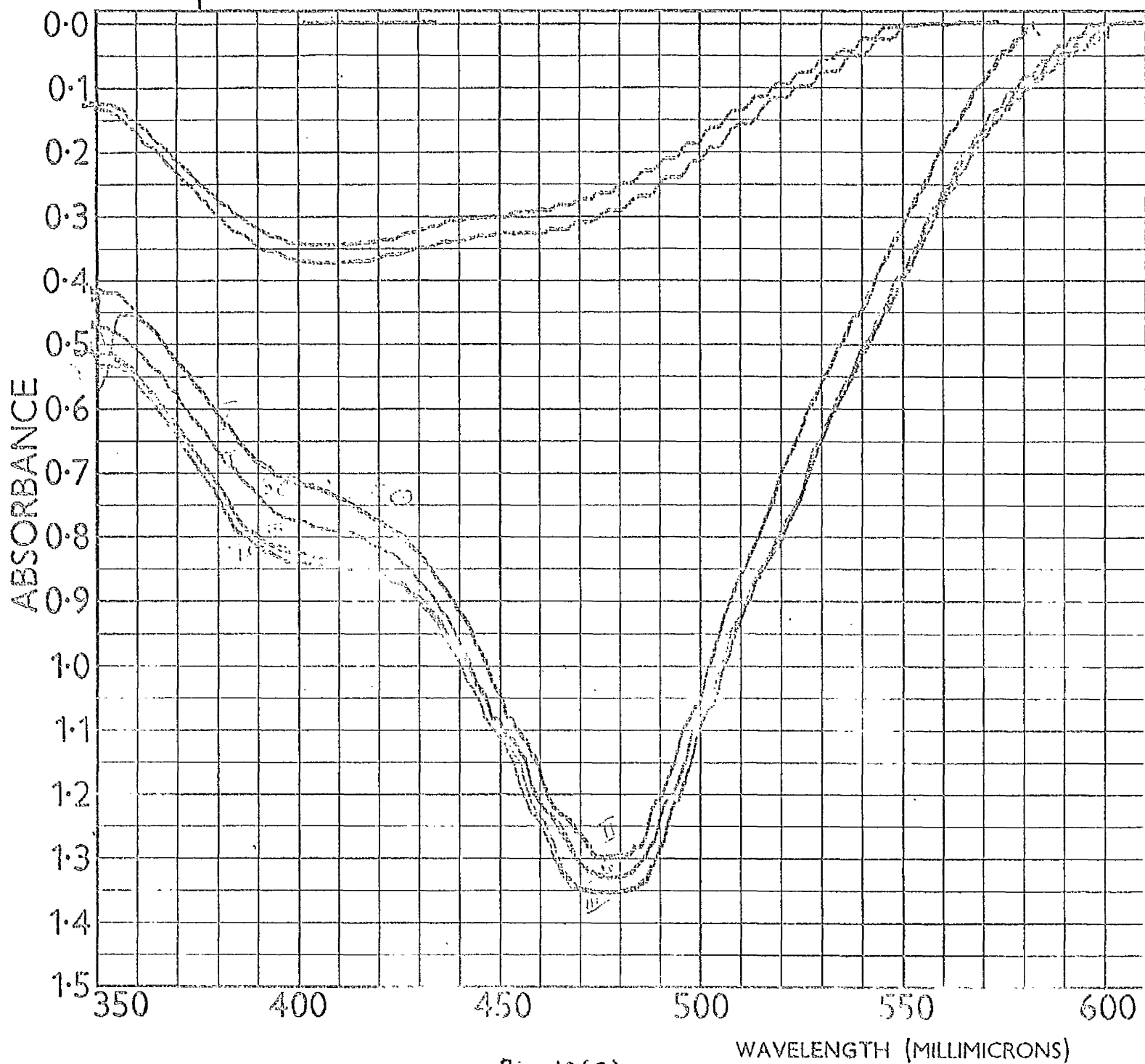
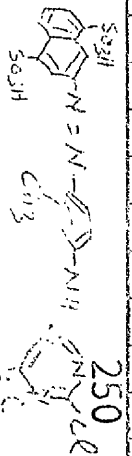
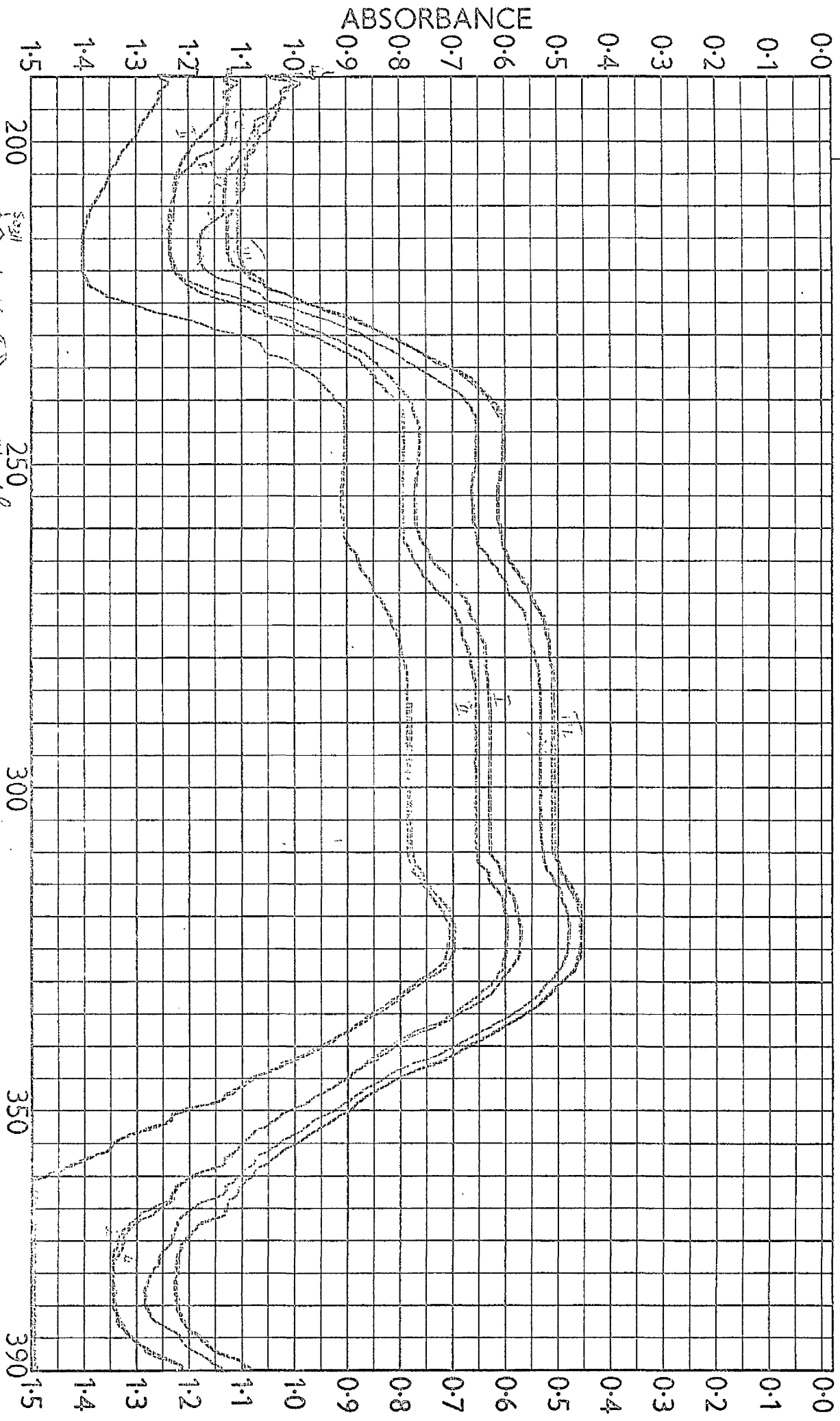


Fig. 12(a)

SAMPLE <u>Dye A</u>	CURVE NO. _____
ORIGIN _____	CONC. _____
SOLVENT <u>Tap water</u>	CELL PATH <u>1 mm</u>
	REFERENCE _____



WAVELENGTH (MILLIMICRONS)
349.13

SAMPLE <u>Dye B</u>	CURVE NO. _____	SCAN SPEED <u>10</u>	OPERATOR <u>13/6/68</u>
ORIGIN _____	CONC _____	SLIT <u>2.5</u>	DATE <u>13/6/68</u>
SOLVENT <u>Talc water</u>	CELL PATH <u>1 cm</u>	REMARKS _____	
REFERENCE _____			

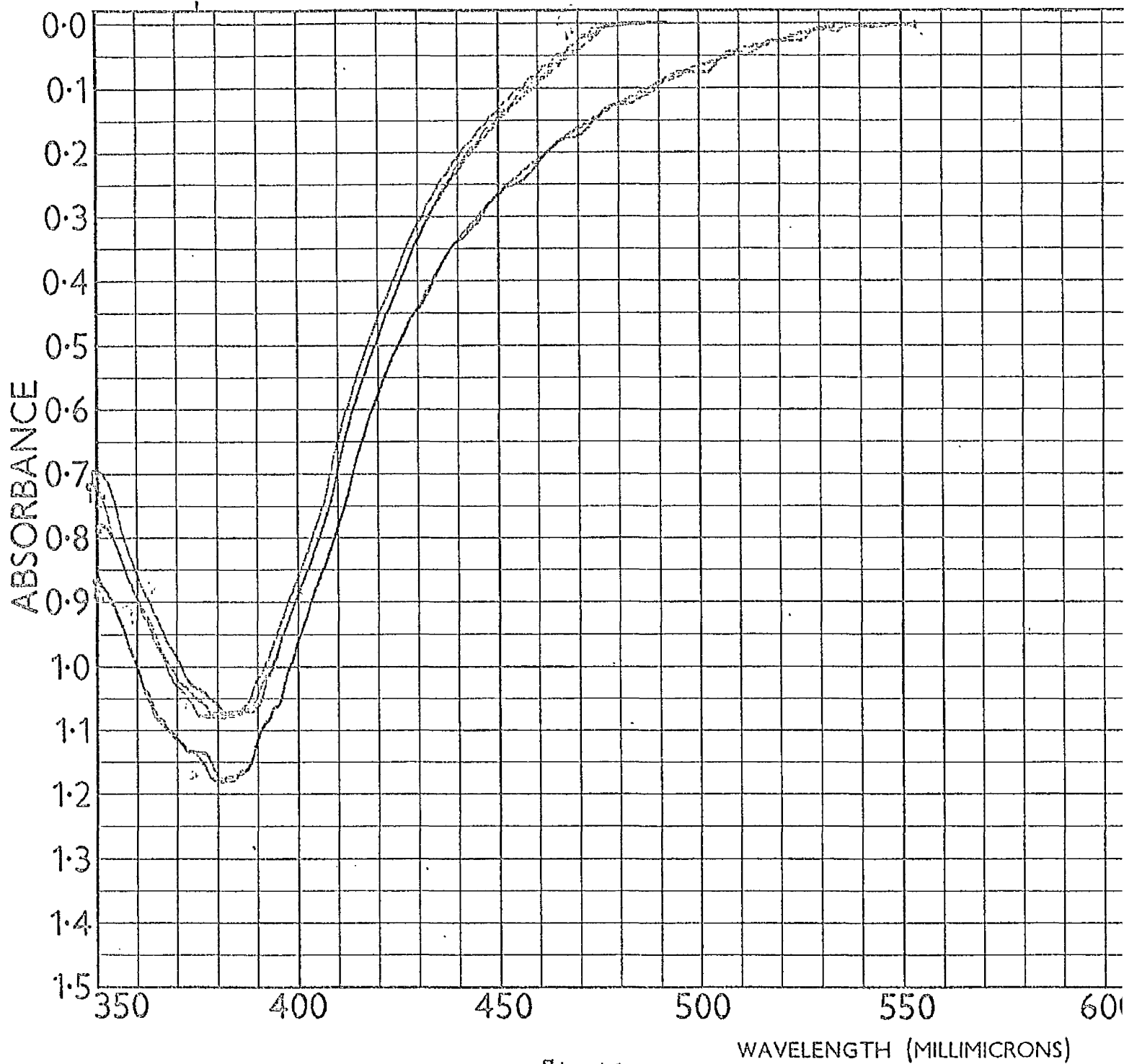


Fig. 14

SAMPLE <u>Dye B</u>	CURVE NO _____
ORIGIN _____	CONC _____
SOLVENT <u>Tap water</u>	CELL PATH <u>1 mm</u>
	REFERENCE _____

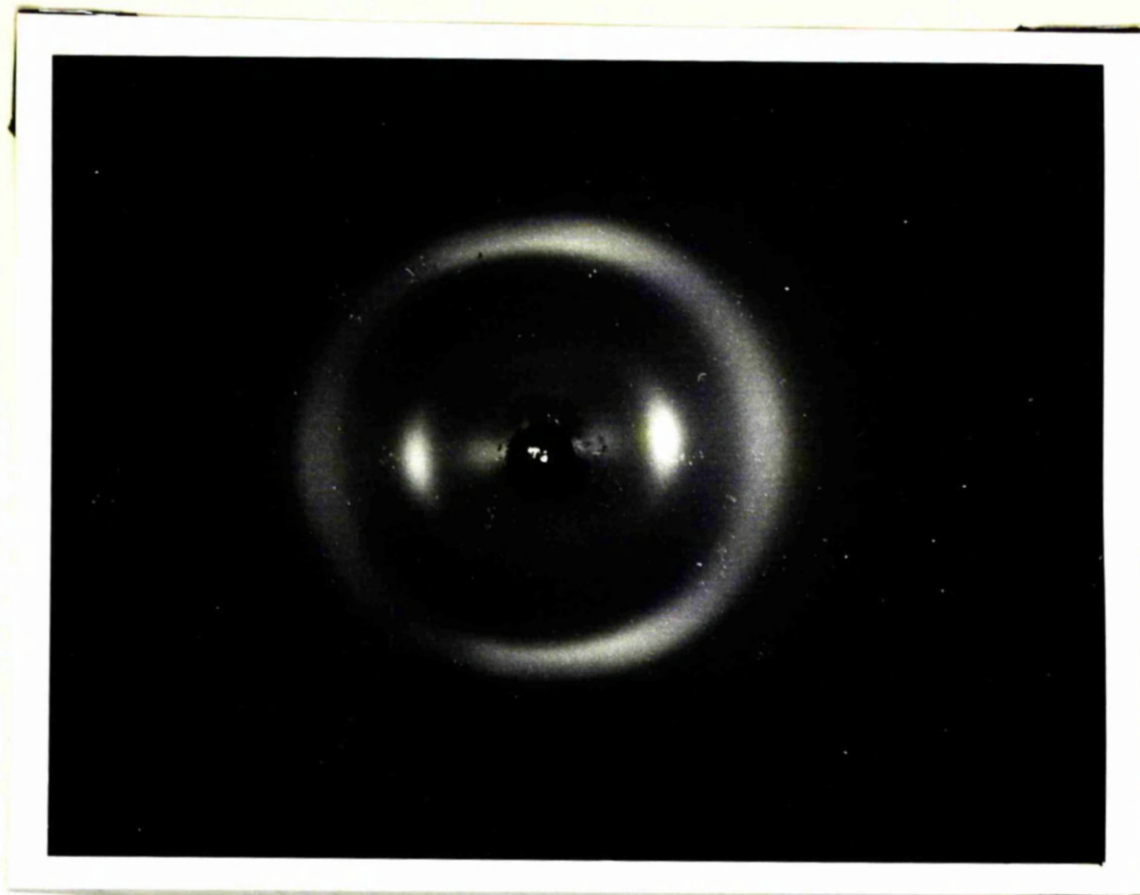


Fig. 15

X-ray photograph of Procion Brilliant Blue H₇G

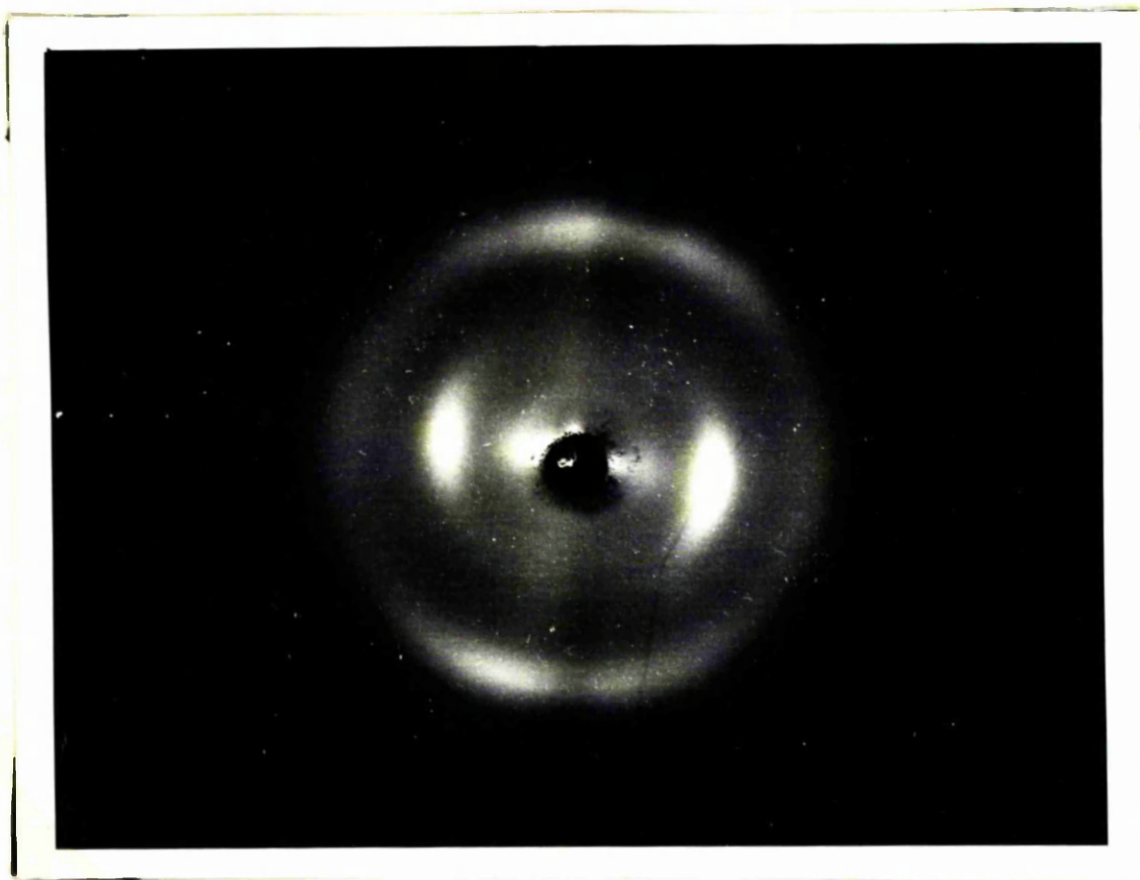


Fig. 16

X-ray photograph of Cellophane

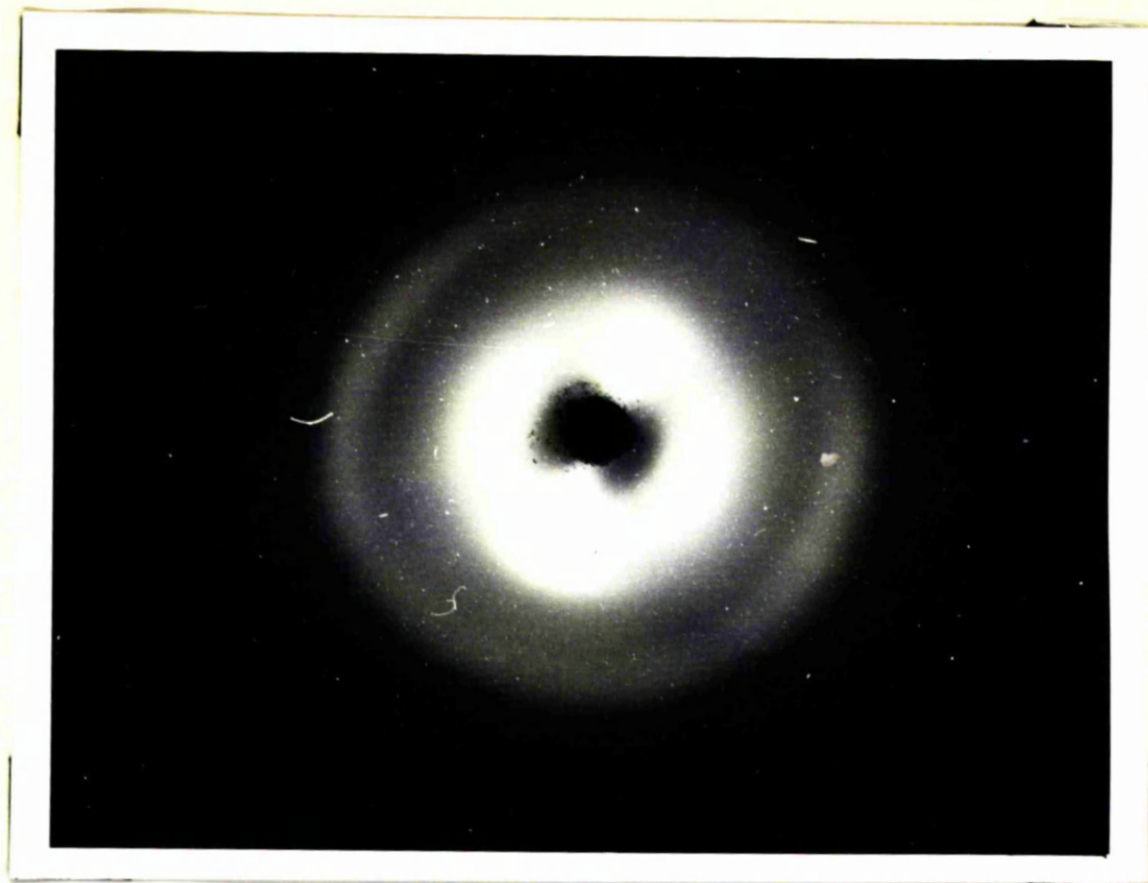


Fig. 17

X-ray photograph of Cellophane dyed (unfixed) with Procion Brilliant Blue H₇G



Fig. 18.

X-ray photograph of Procion Brilliant Blue H₇G

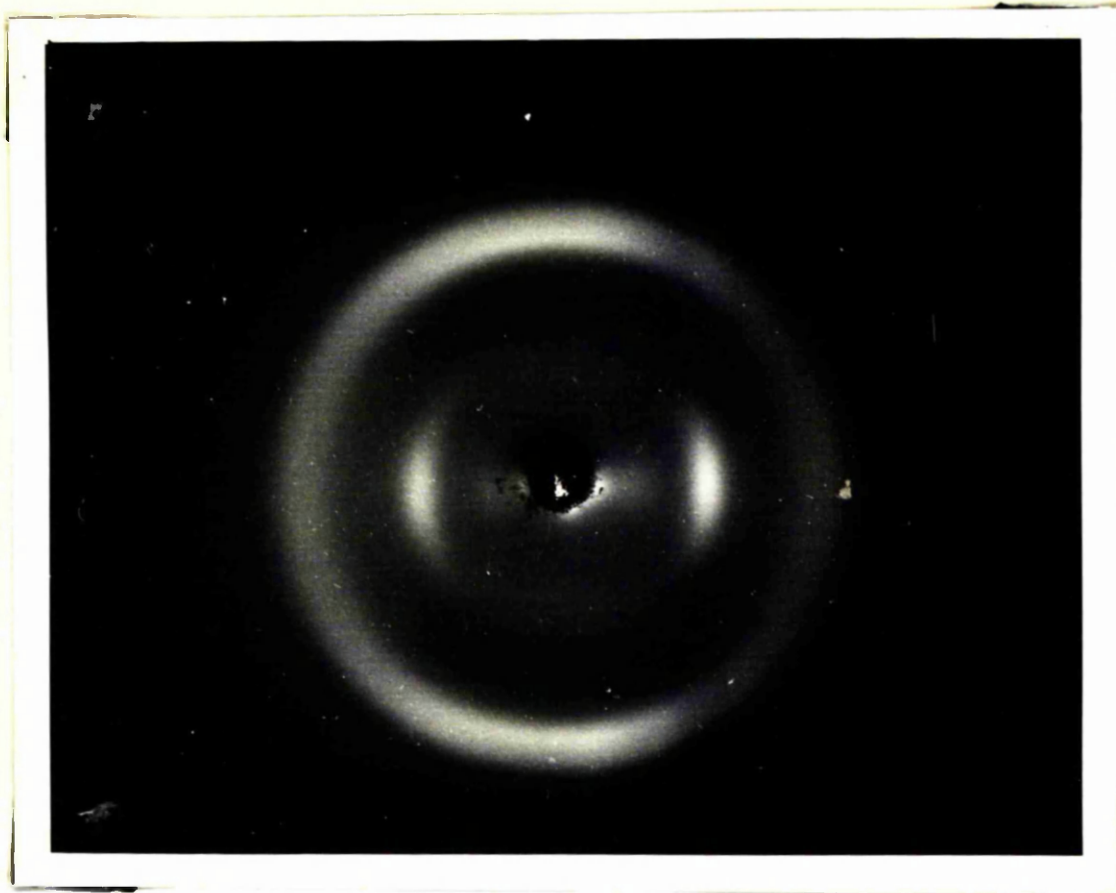


Fig. 19

X- ray photograph of Cellophane dyed (fixed) with Procion Brilliant
Blue H₇G

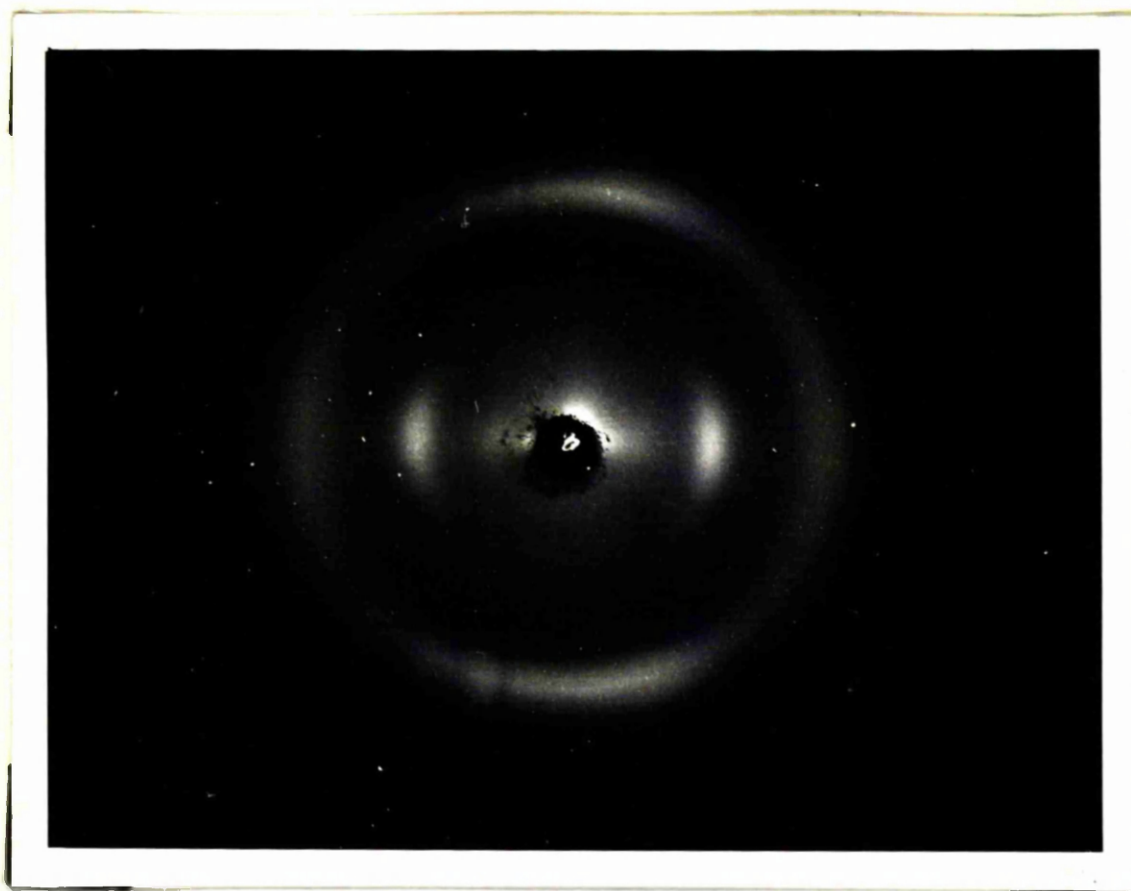


Fig. 20

X-ray photograph of Cellophane dyed (fixed) with Procion Brilliant
Blue H-C

WAVELENGTH (MILLIMICRONS)

319.21

SAMPLE	Pentachloro 11-65	
ORIGIN		
SOLVENT	Pentachloro	
CURVE NO.		
CONC		
CELL PATH		
REFERENCE		
SCAN SPEED	Fast	OPERATOR
SLIT	25	DATE
REMARKS	No. 10-10-65	

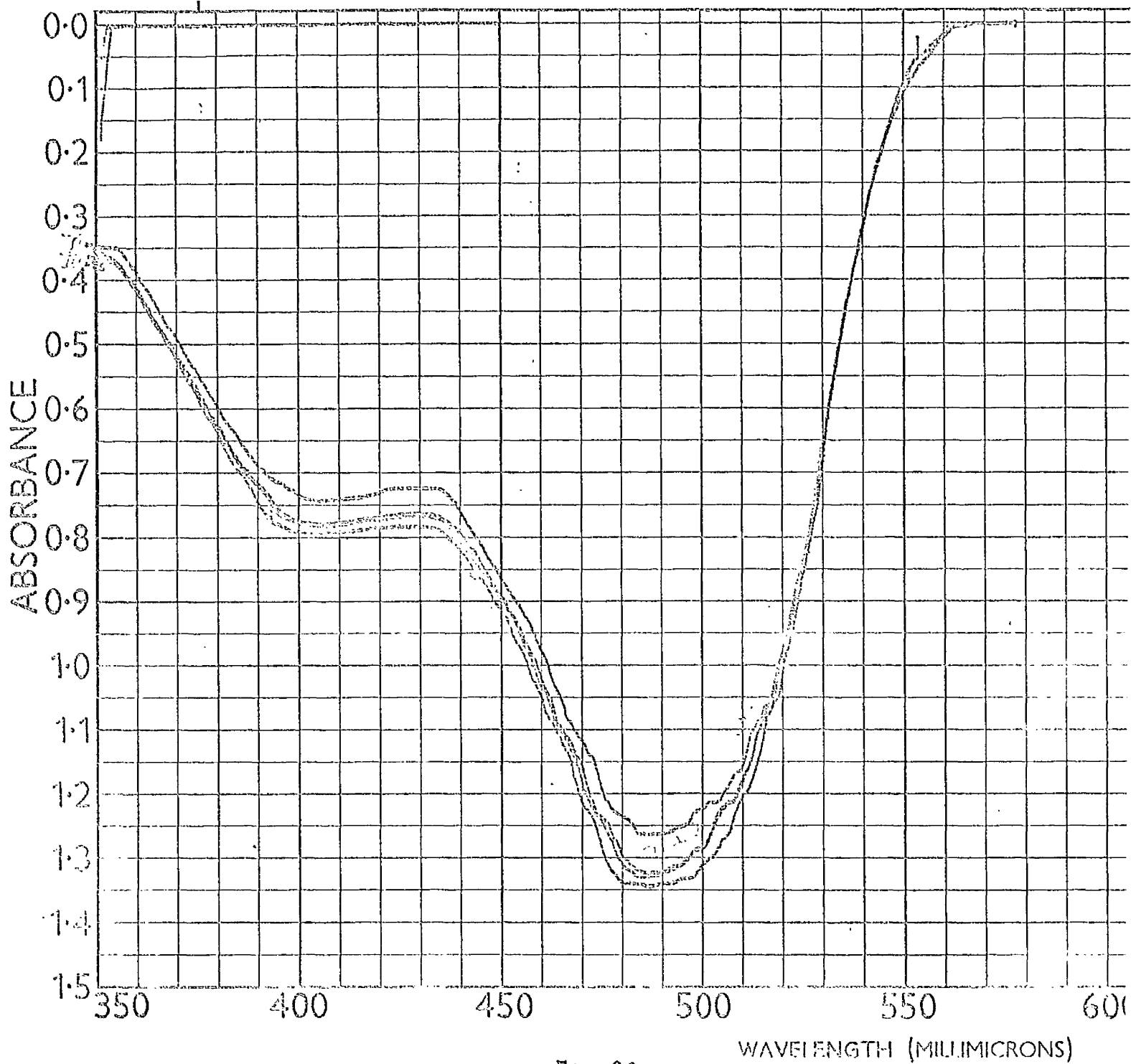


Fig. 22

SAMPLE <u>Proc. Bull. 10-11-68</u>	CURVE NO _____
ORIGIN _____	CONC _____
SOLVENT <u>Tap water</u>	CELL PATH _____
	REFERENCE _____

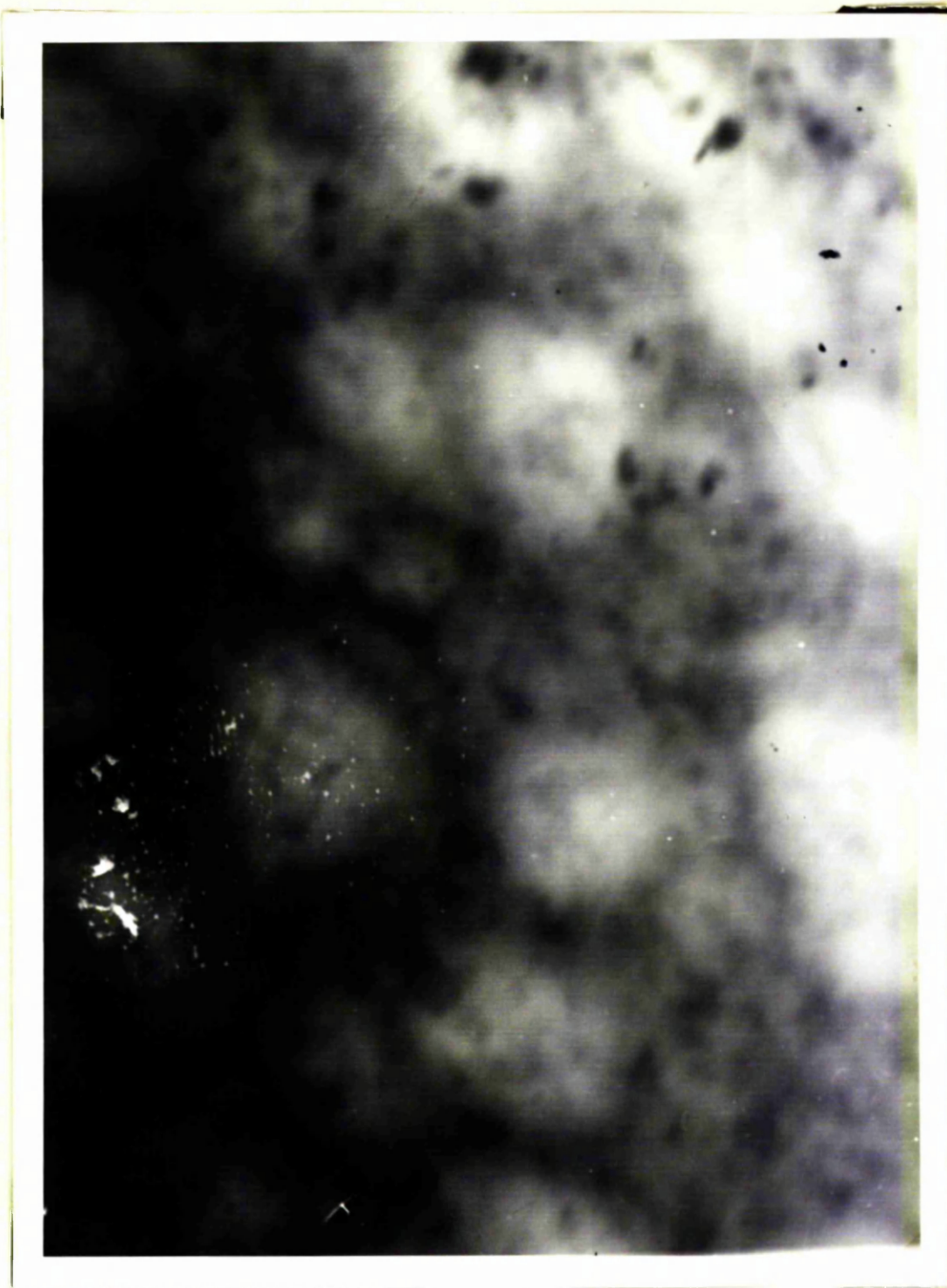


Fig. 25

Electron micrograph of cellulose film dyed (fixed) with Procion Brilliant Orange E-6B, showing the presence of dye aggregates and high porosity of the film. (Magnification 50,000).

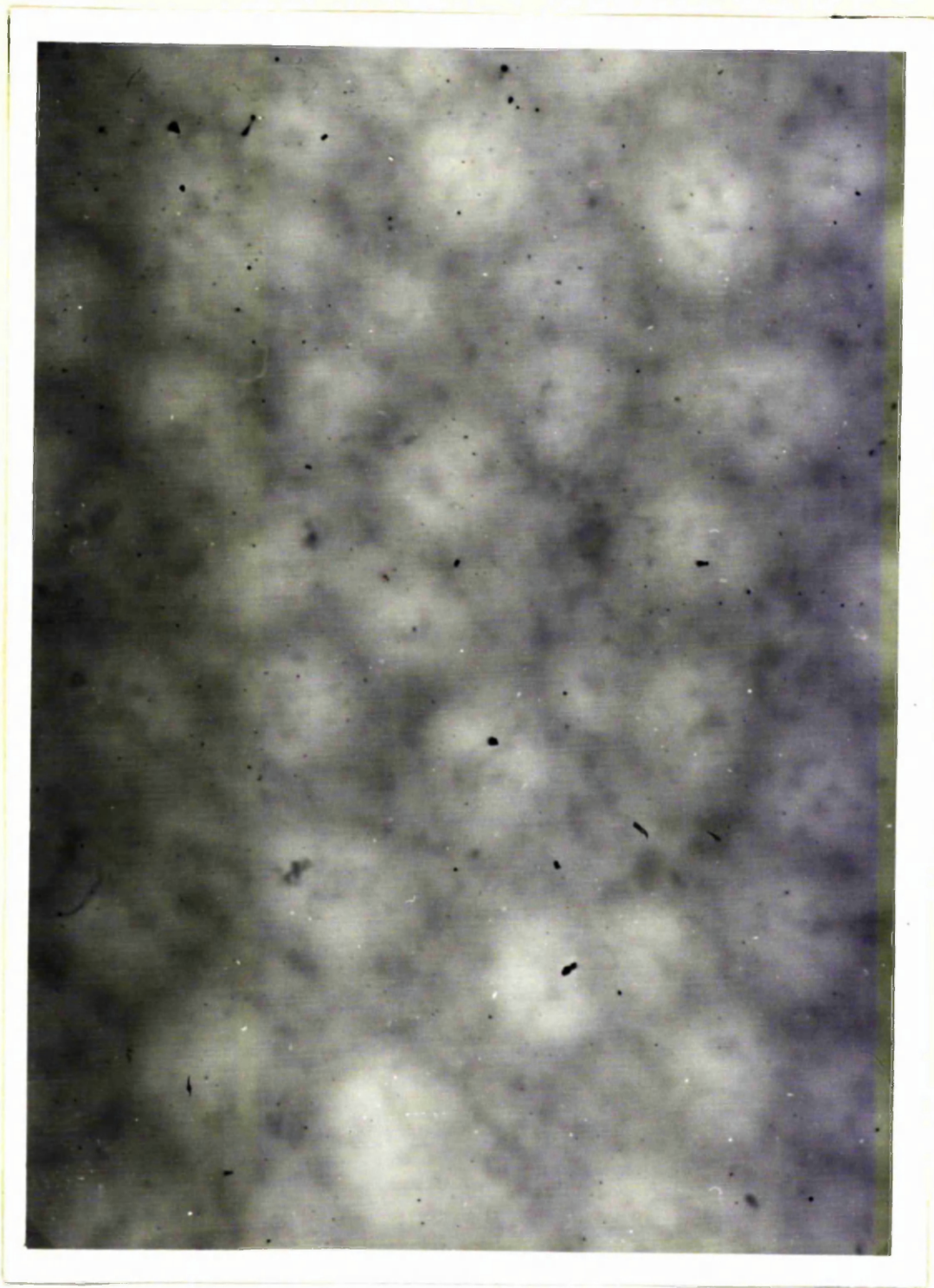


Fig. 26

Electron micrograph of cellulose film dyed (fixed) with Procion Brilliant Orange M-GS, showing the presence of dye aggregates and high porosity of the film. (Magnification 30,000).

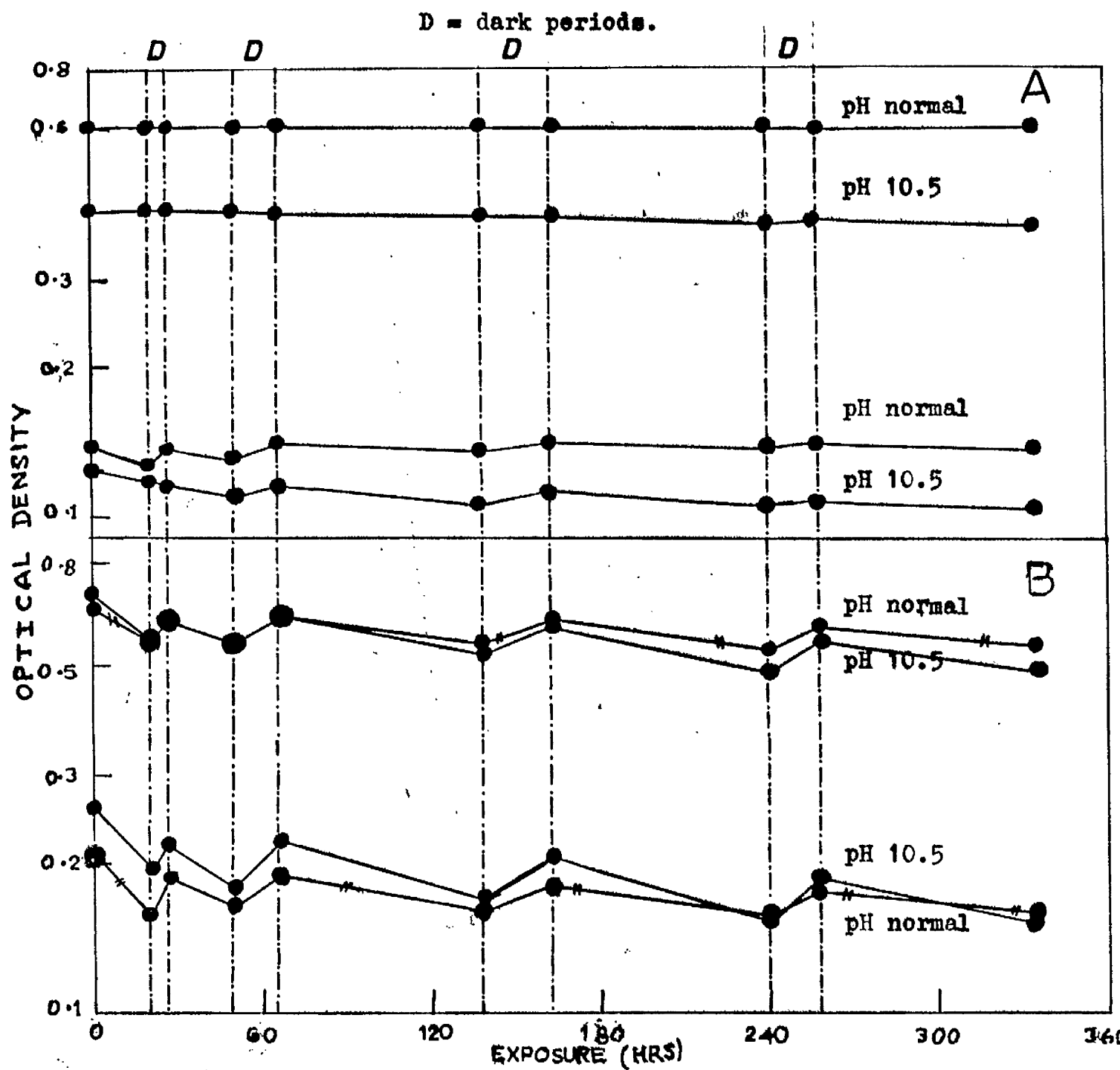


Fig. 24 Effect on dyed Cellophane fading rates, of alternating irradiation and storage in the dark. Dye used is C.I. Direct Green 26.

(A) $\lambda_{\max} 620 \text{ m}\mu$; (B) $\lambda_{\max} 405 \text{ m}\mu$.

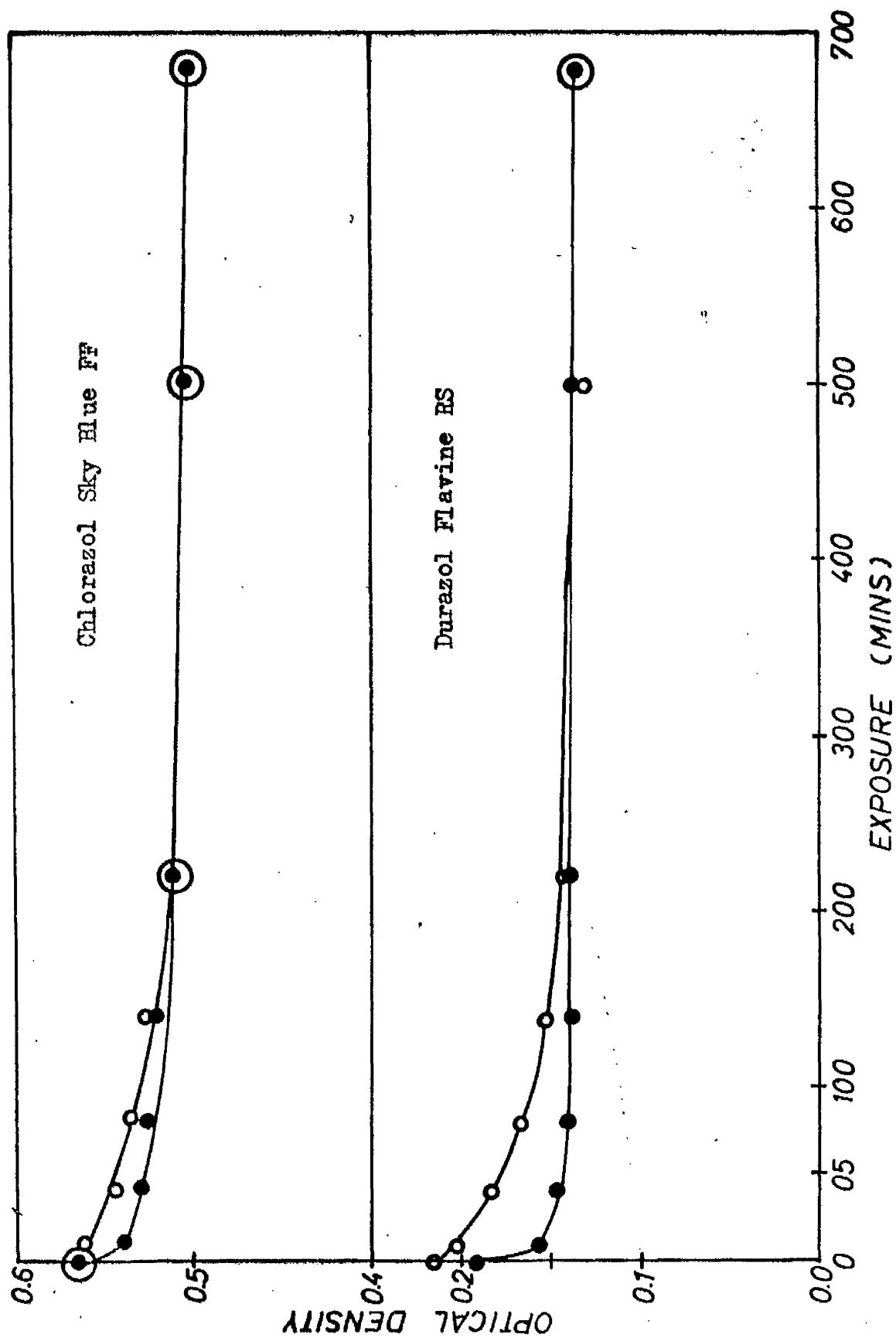


Fig. 28 Fading of Chlorazol Sky Blue F.F. and Durazol Flavine R.S. in glass slides and in open exposures. O Glass; ● Metal.

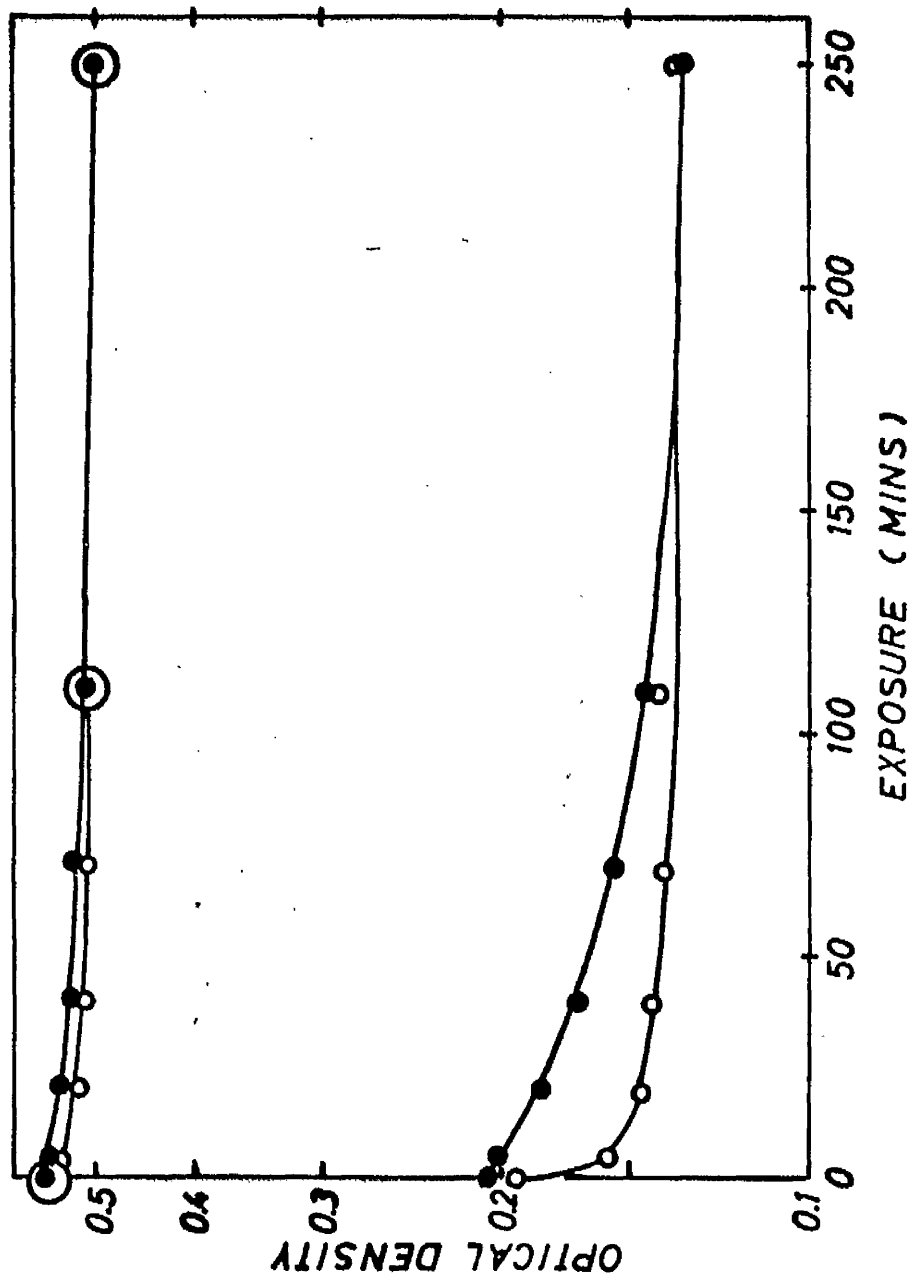
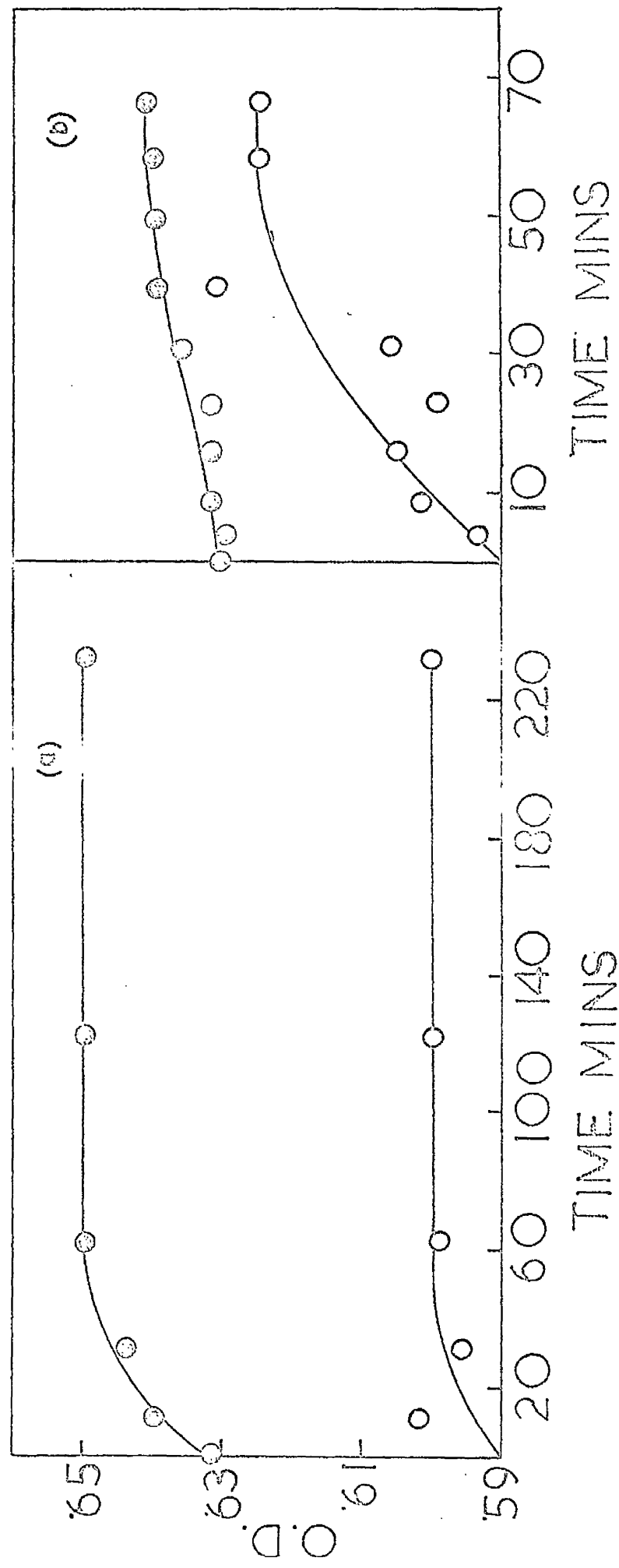


Fig.29 Fading of Chlorazol Sky Blue FF and Durazol Flavine RS in glass slides and in open exposures. \circ Glass; \bullet Metal.



○---GLASS SLIDE

○---METAL SLIDE

Fig. 30 Fading of Azo dyes (p-quinonoid) in the laboratory) on Cellophane film, sandwiched between glass slides and in open exposures.

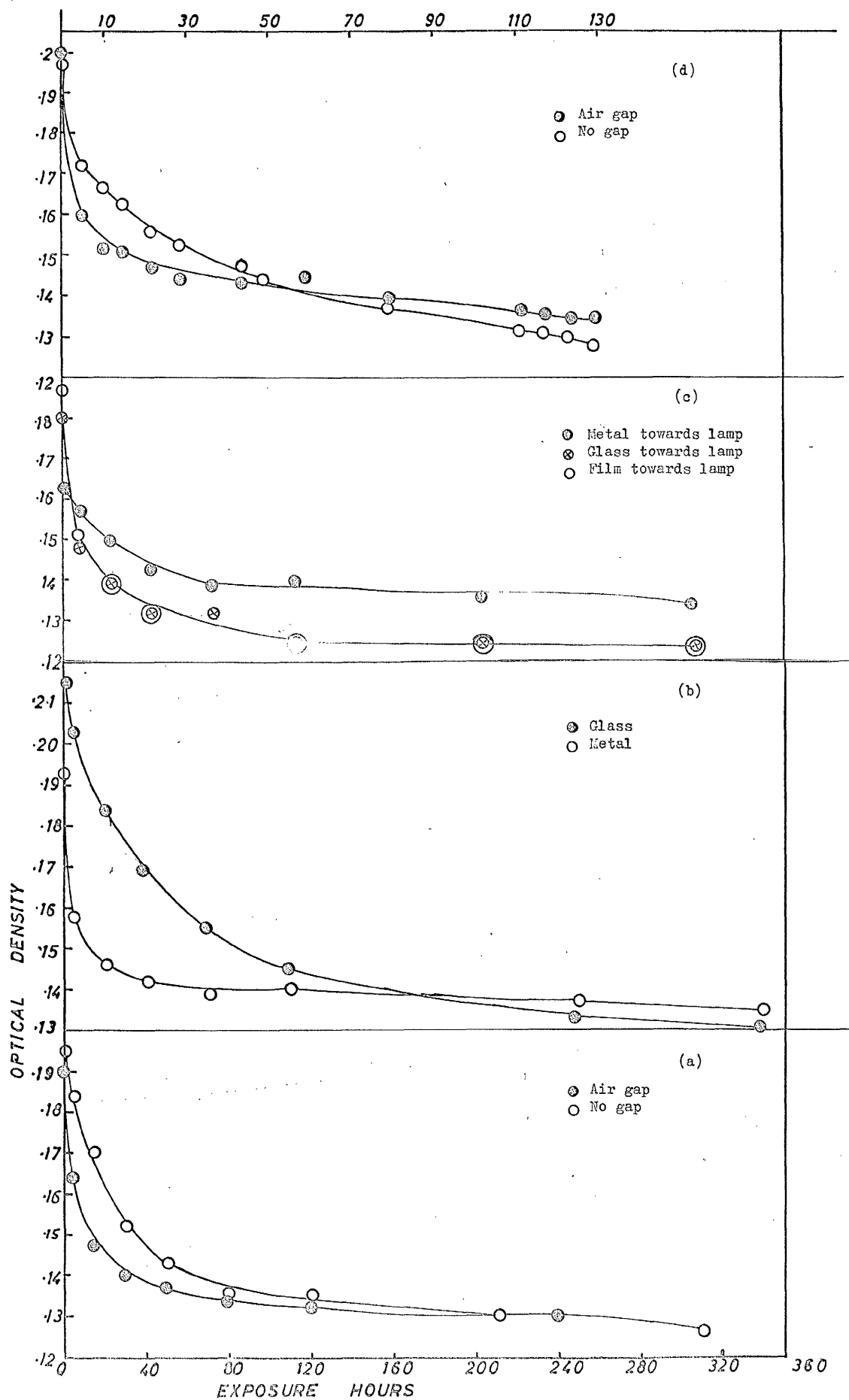


Fig. 31 Fading of Benzal Flavine RS:

(a & d) Films between the glass slides with and without an air gap,

(b) films sandwiched in glass slides and in open exposure, and

(c) same as in Fig. 32c.

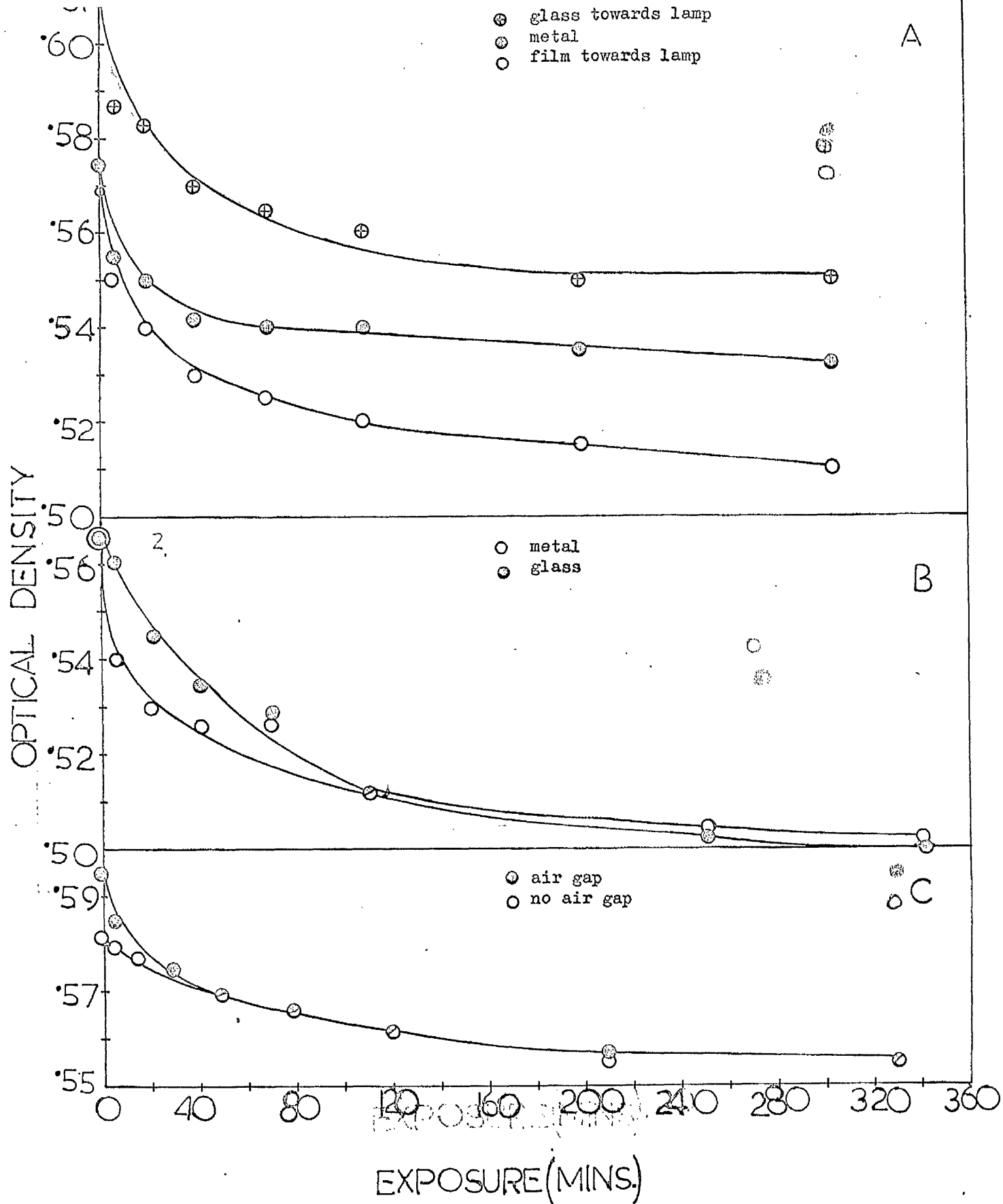


Fig.32 Fading of Chlorazol Sky Blue FF

- (a) films between the glass slides with and without an air gap
 (b) films sandwiched in glass slides and in open exposure (metallic slides)
 (c) film towards the light source and the glass plate at its back; film at the back of the glass plate (the latter being towards the light source); film in open on metallic slides.

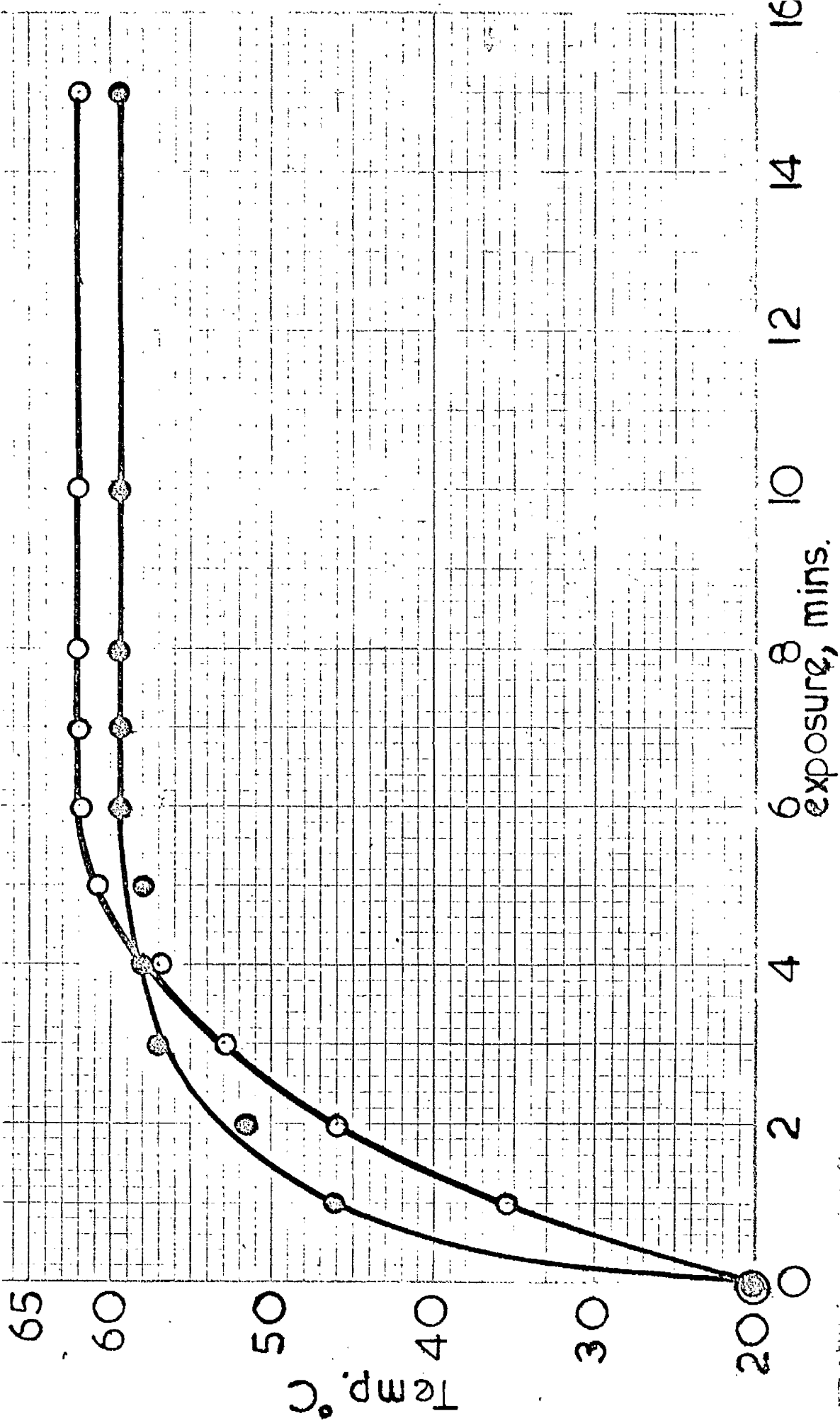


Fig.33 Rise in temperature on exposure to mercury fading lamp.

- Glass.
- Metal.

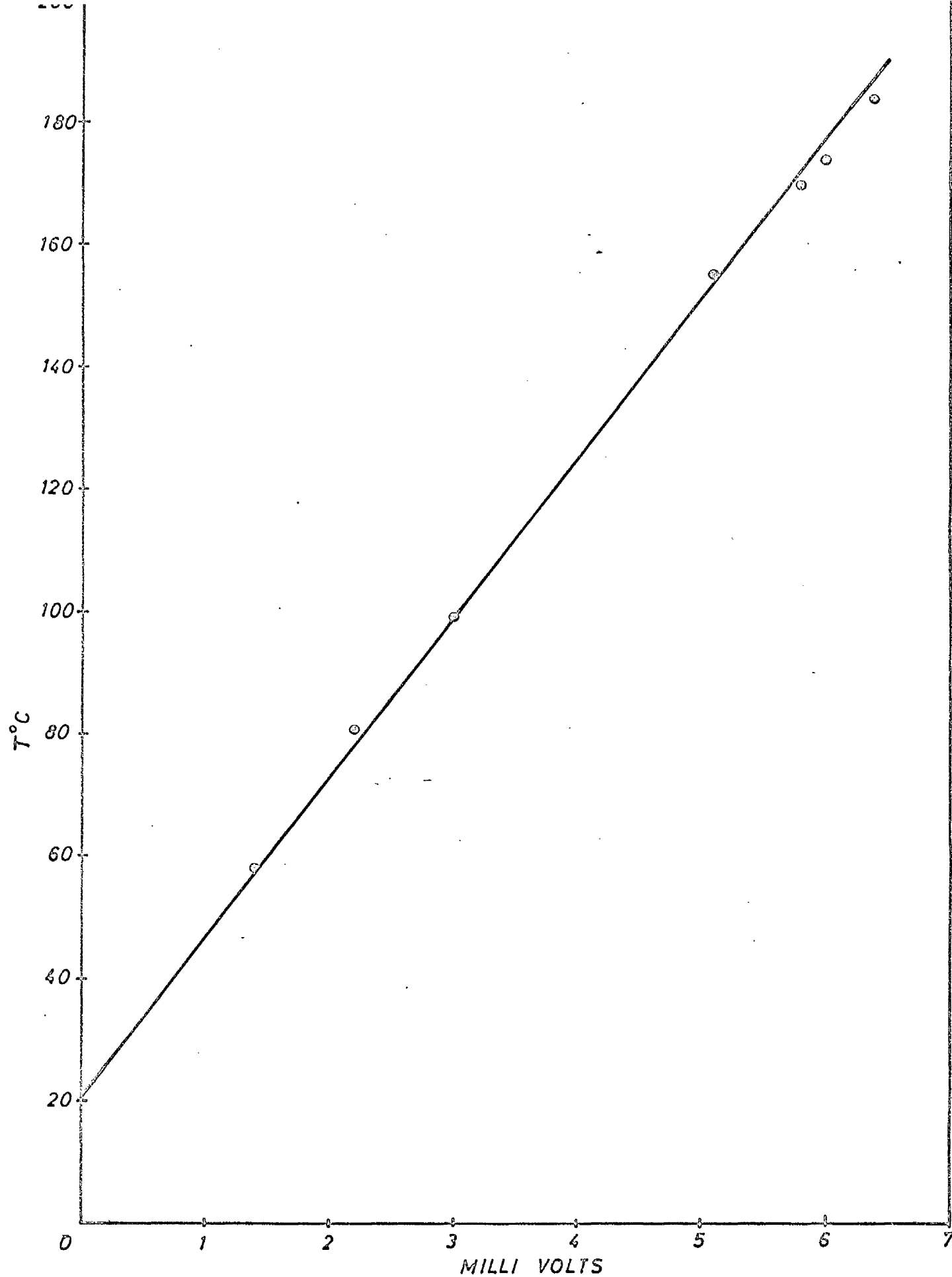


Fig.34 Calibration curve: Temperature against millivolts.

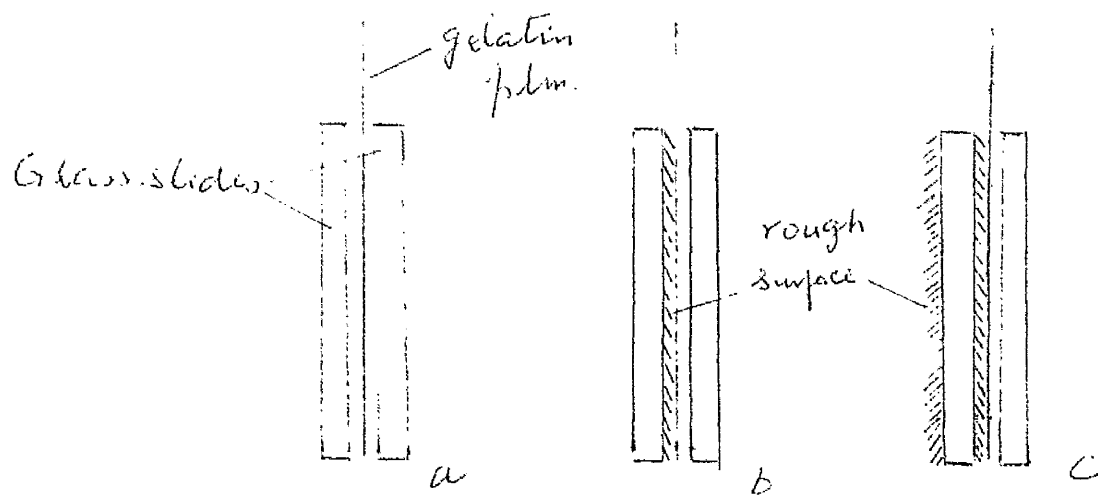


Fig. 35 Showing gelatin films (plain and rough)

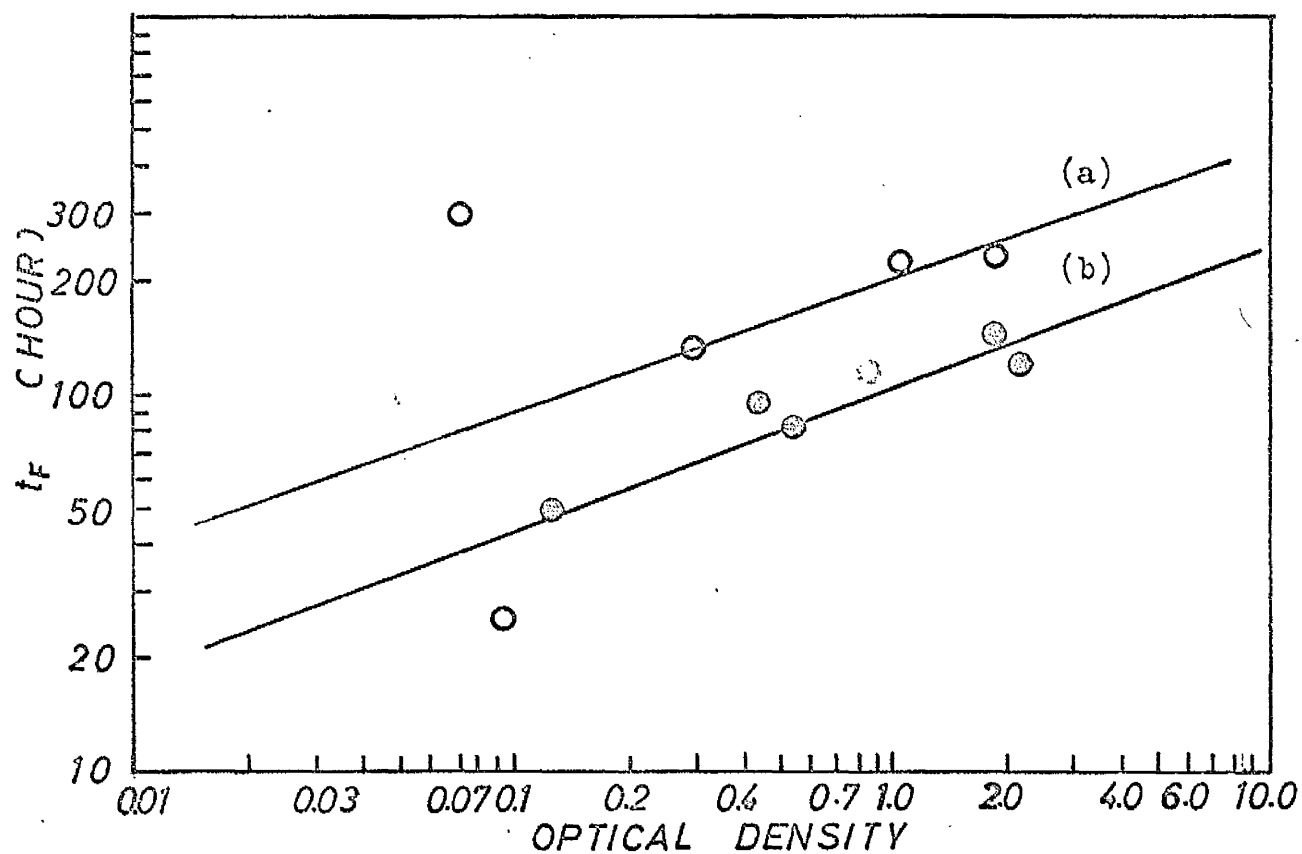


Fig.36 CF curves of Procion Brilliant Orange M-GS on Cellophane.

- (a) Fixed.
- (b) Unfixed.

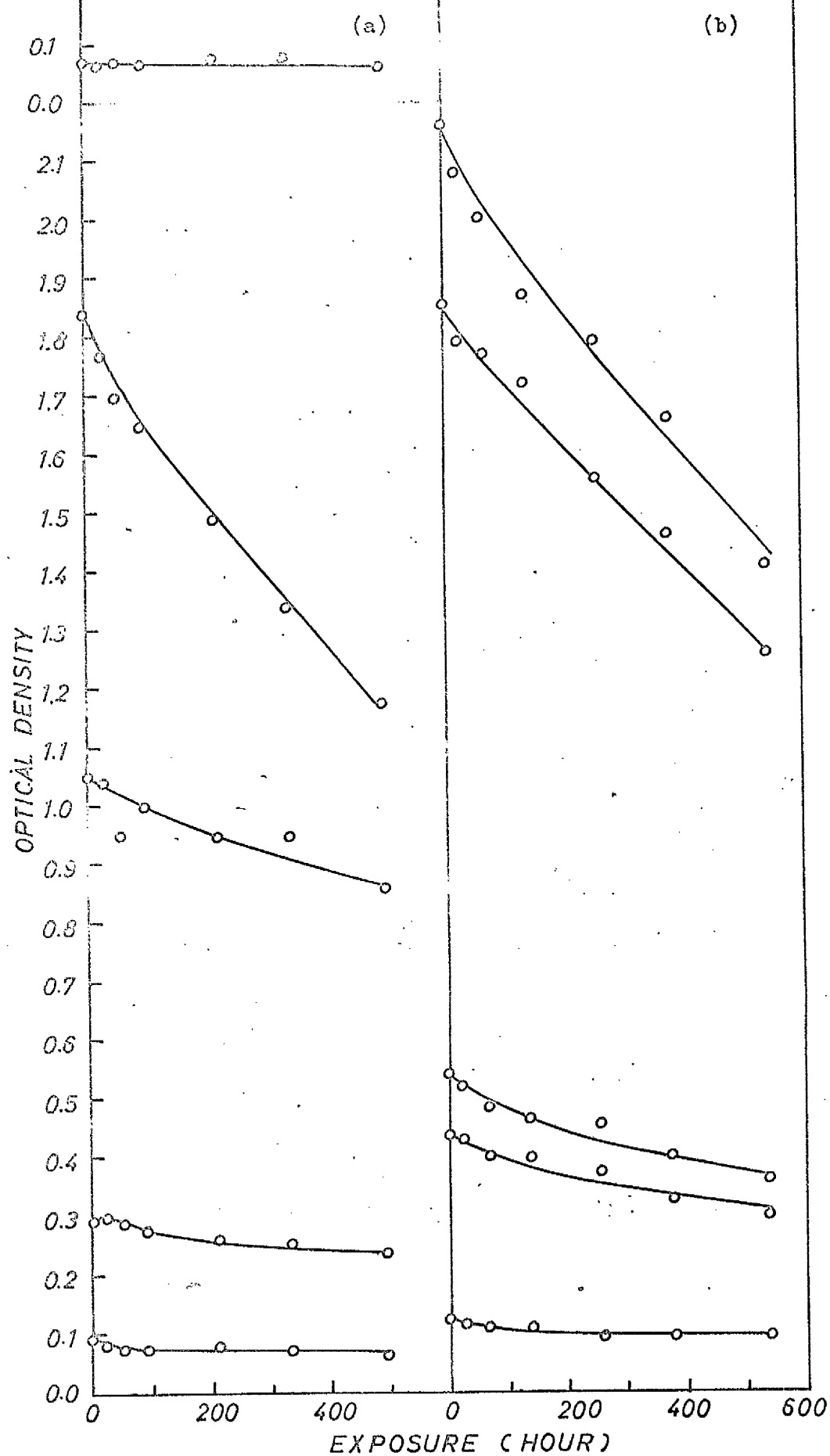


Fig. 37 Fading rate curves of Procion Brilliant Orange M - GS on Cellophane.

(a) Fixed.

(b) Unfixed.

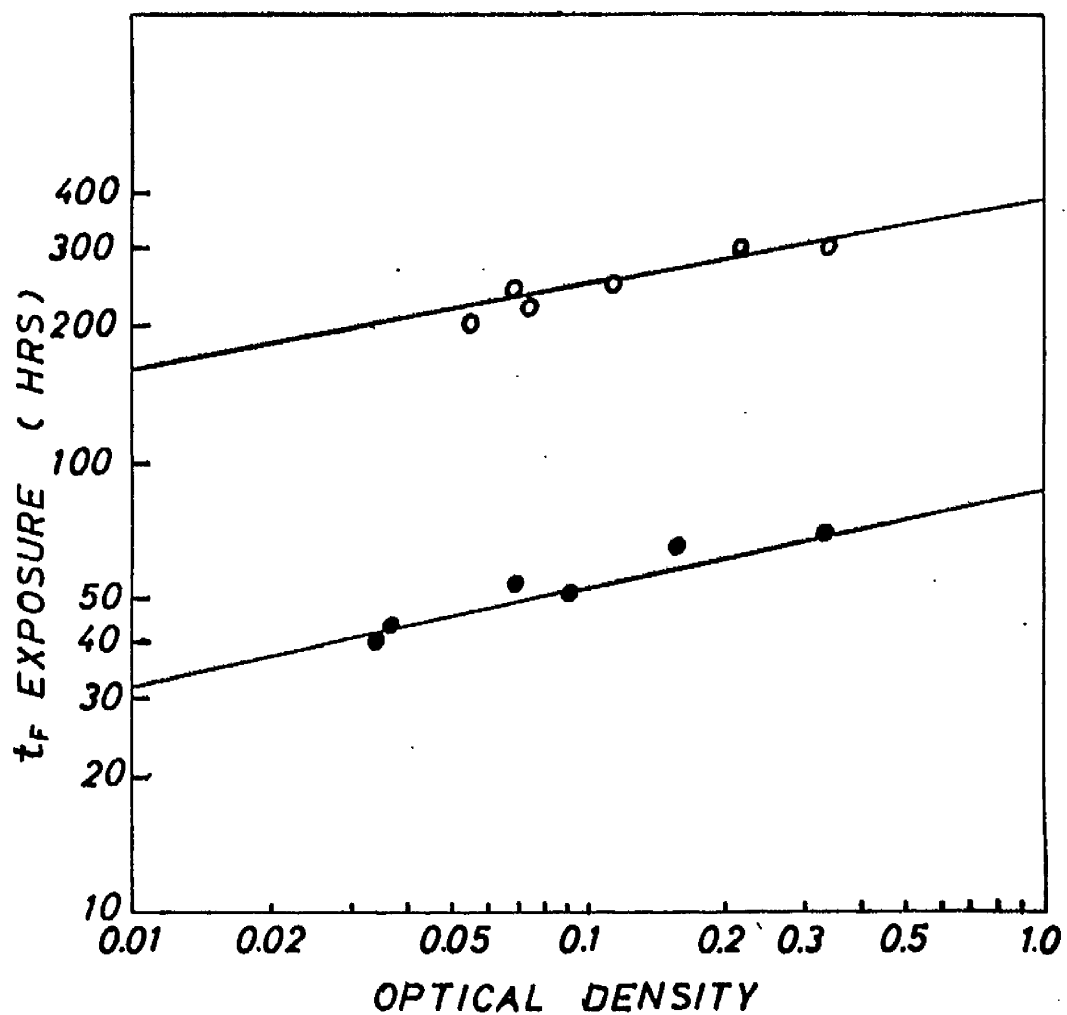


Fig.38 CF curves for Procion Brilliant Yellow 6G on Cellophane.

- Fixed.
- Unfixed.

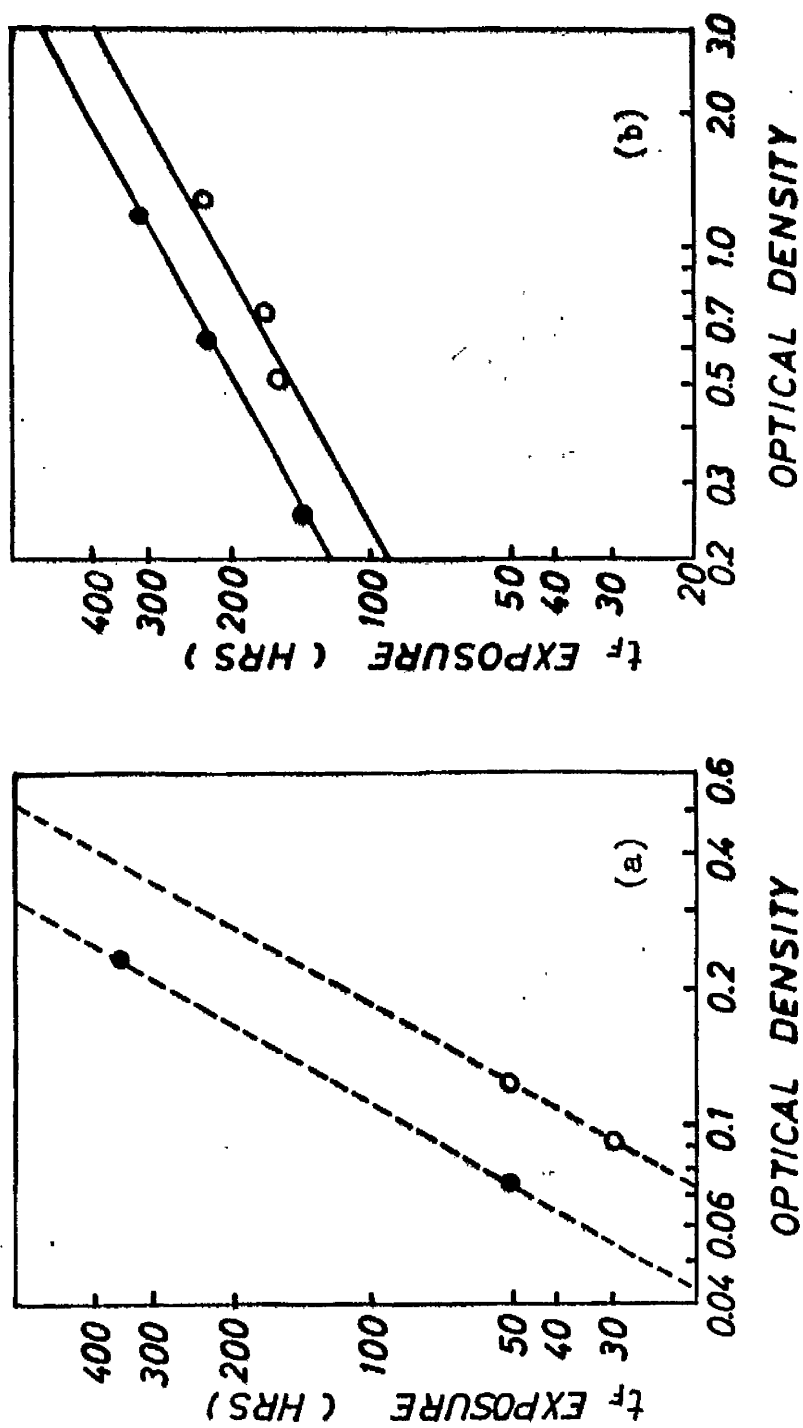


Fig. 39 Characteristic fading curves (CF curves) for:

(a) Procion Blue 3G, and

(b) Procion Brilliant Red M - 5BS,

on Cellophane.

● Fixed.

○ Unfixed.

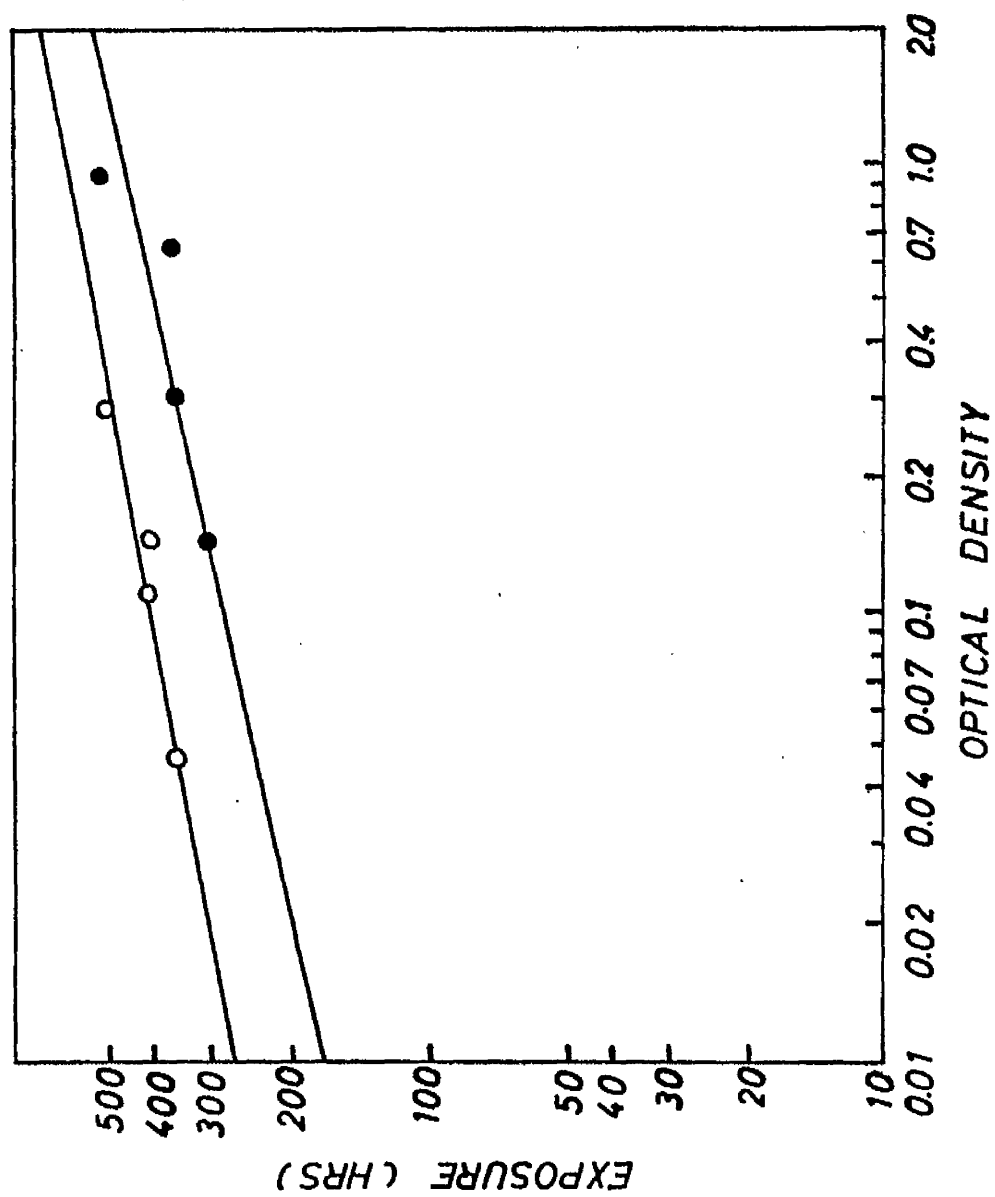


Fig. 40 CF curves of Procion Brilliant Blue H7G on Cellophane.

- Fixed.
- Unfixed.

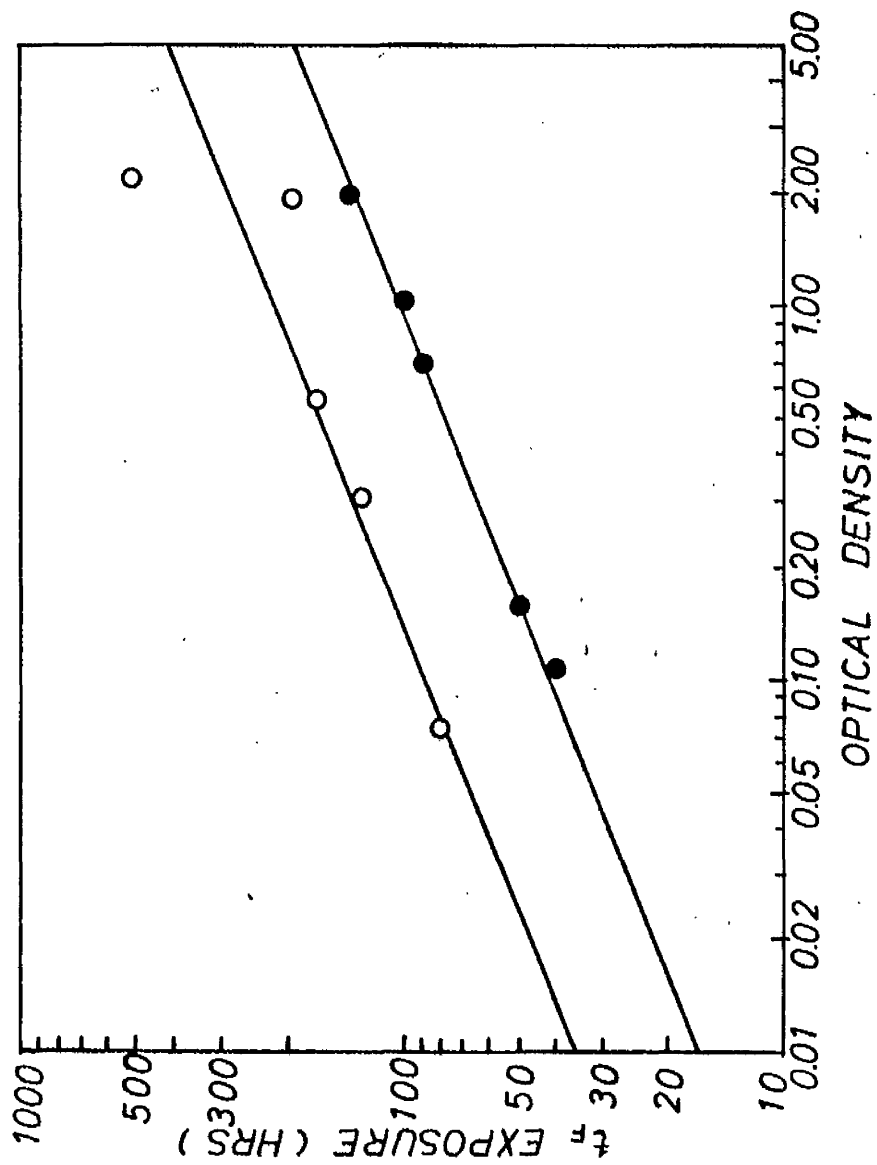


Fig. 41 CF curves of Procion Brilliant Orange G on Cellophane.

○ Fixed.

● Unfixed

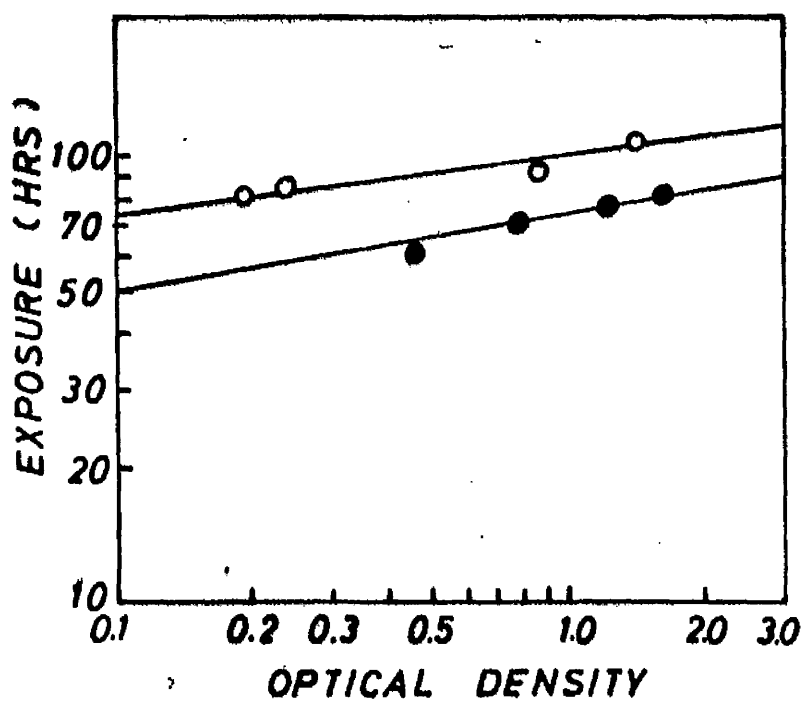


Fig. 42 CF curves of Procion Brilliant Orange M - GS on Cellophane.

- Fixed.
- Unfixed. (hydrolysed before dyeing)

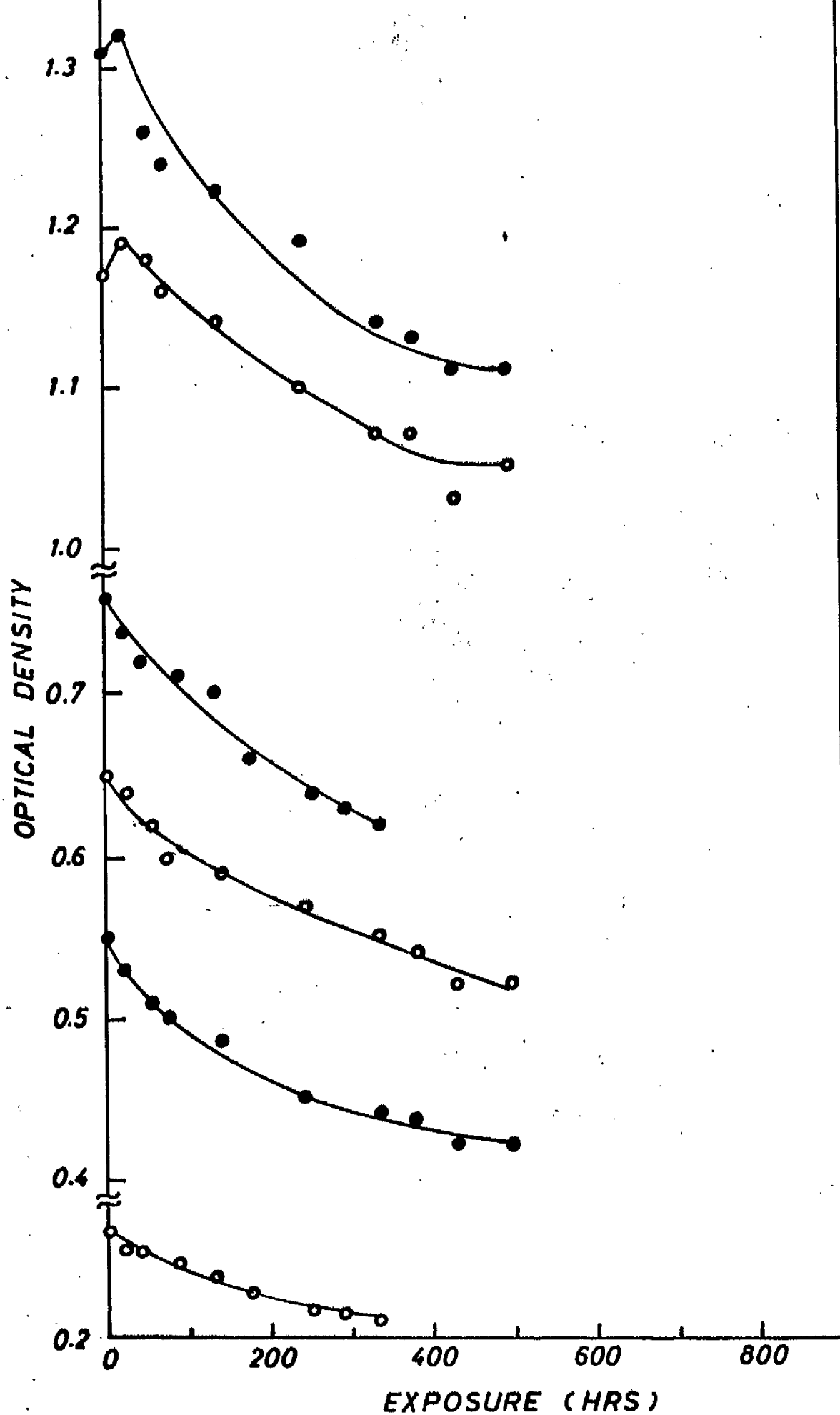


Fig.43 Fading rate curves of Procion Brilliant Red M-5BS on Cellophane. ○ Fixed; ● unfixed.

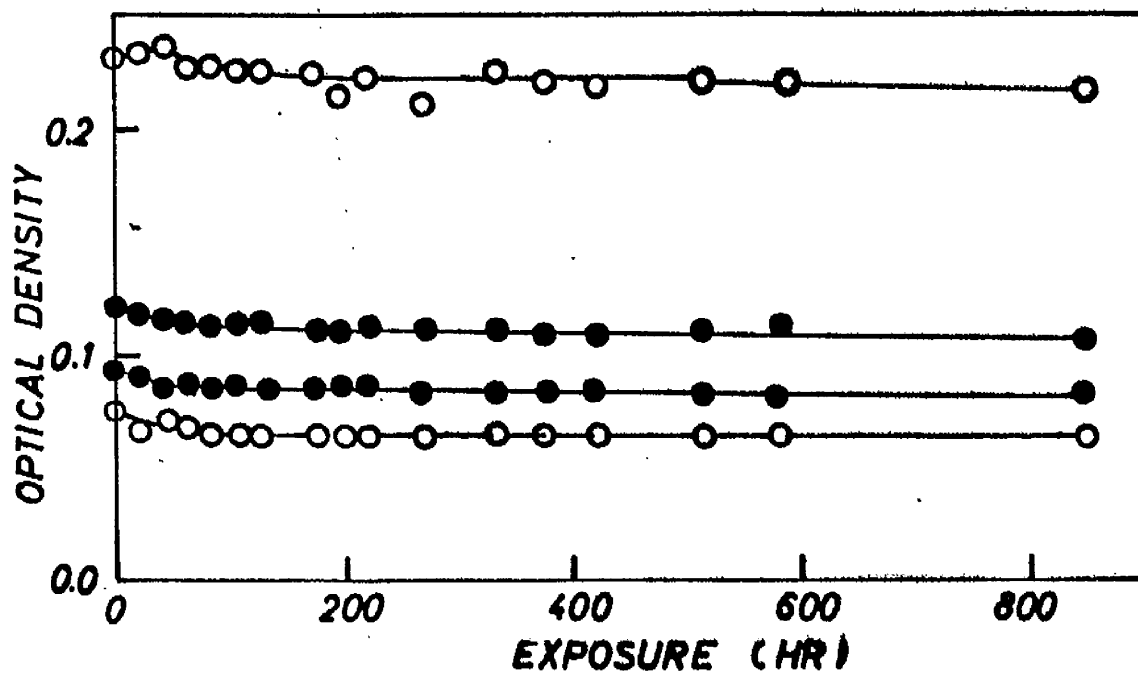


Fig. 44 Fading rate curves of Procion Blue 30 on Cellophane.

- Fixed.
- Unfixed.

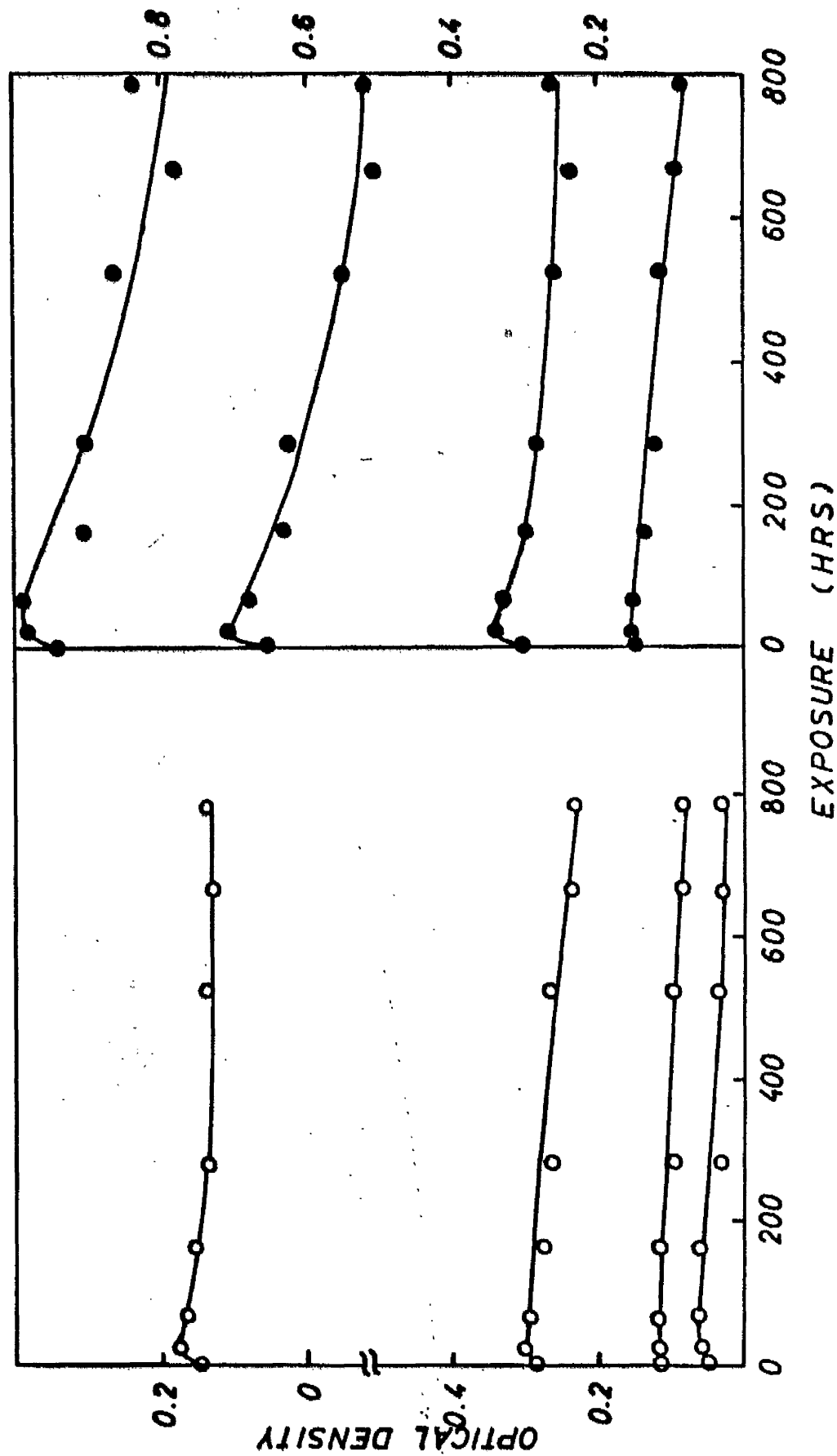


Fig.45 Fading rate curves of Procion Brilliant Blue H7G on Cellophane.

○ Fixed.
● Unfixed.

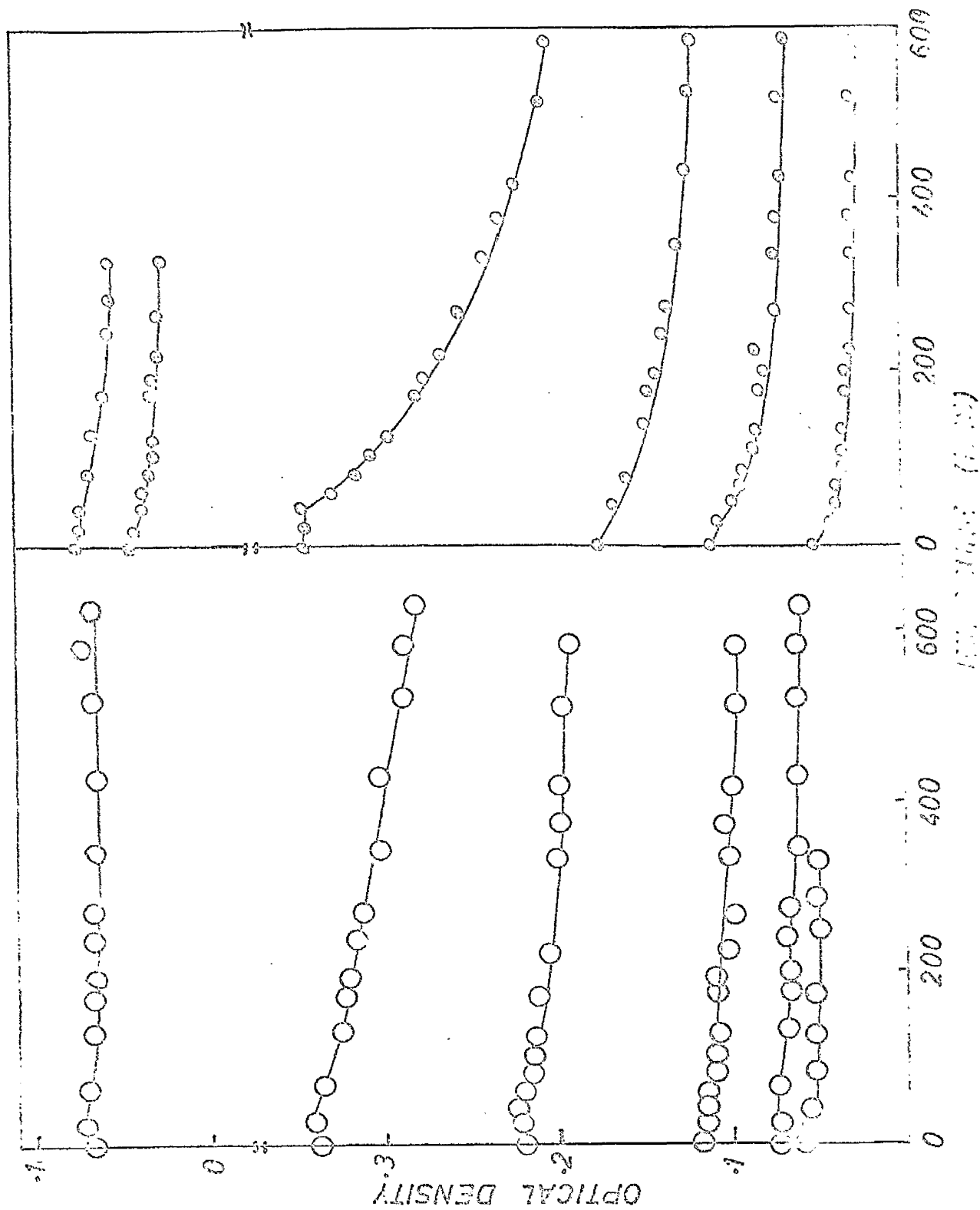


Fig. 46 Rotting curves for Collophane Yellow 6G on Collophane.
 ○ Fixed.
 ⊗ Unfixed.

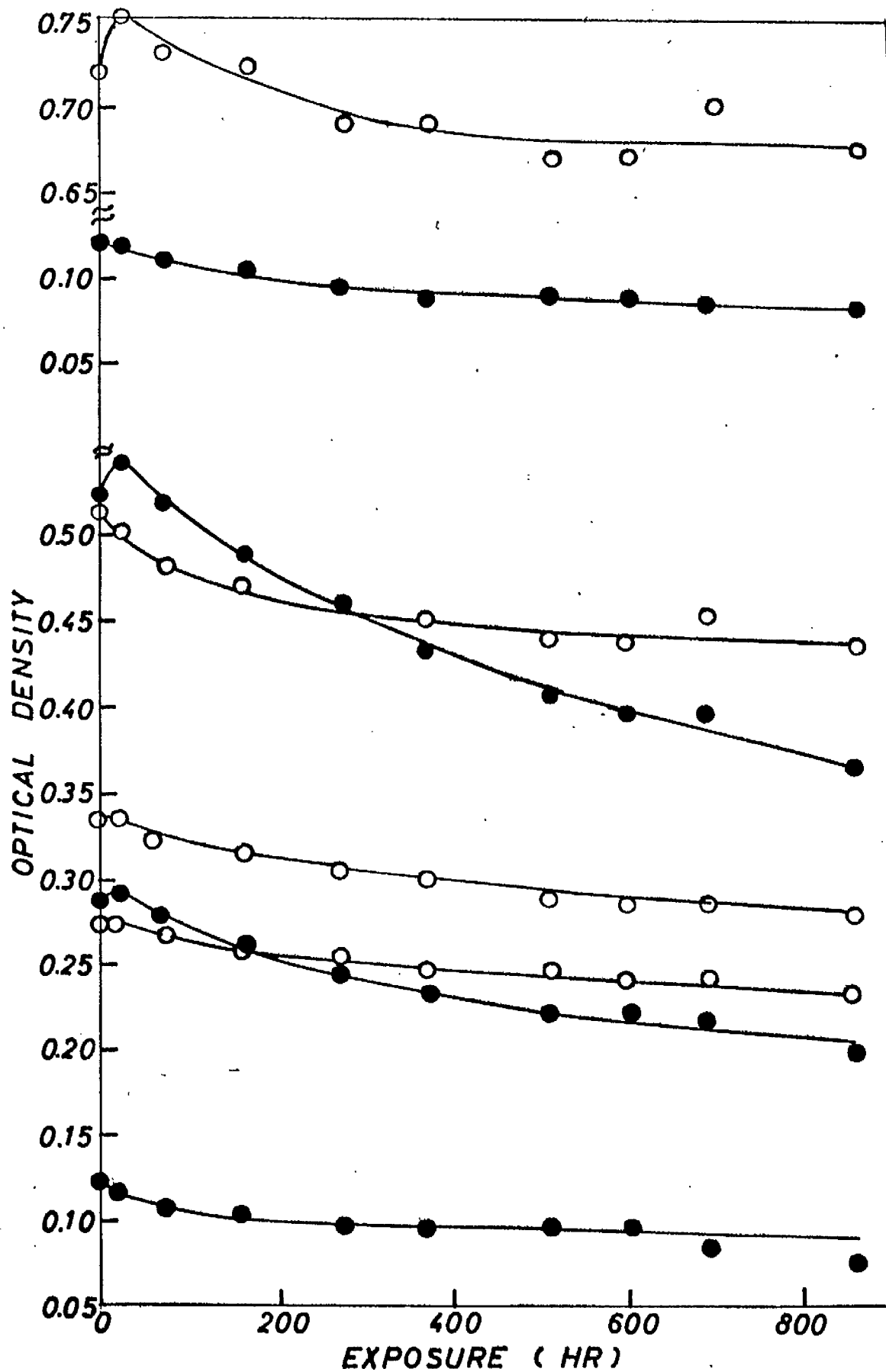


Fig.46(a) Fading rate curves of Procion Brilliant Yellow 6G on gel Cellophane.

○ Fixed.
● Unfixed.

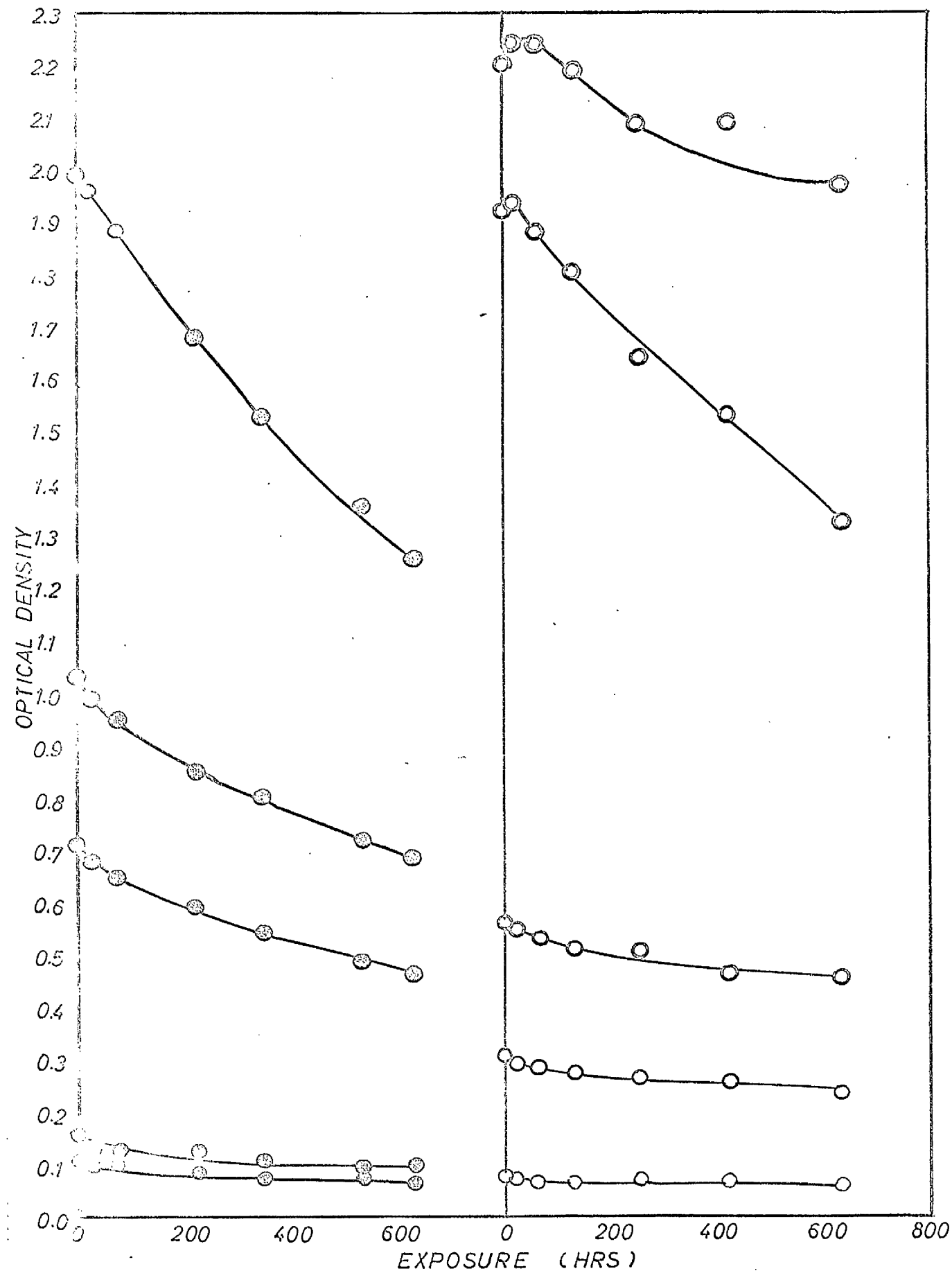


Fig. 47 Fading rate curves of Procion Brilliant Orange G on Cellophane.

- Fixed.
- Unfixed.

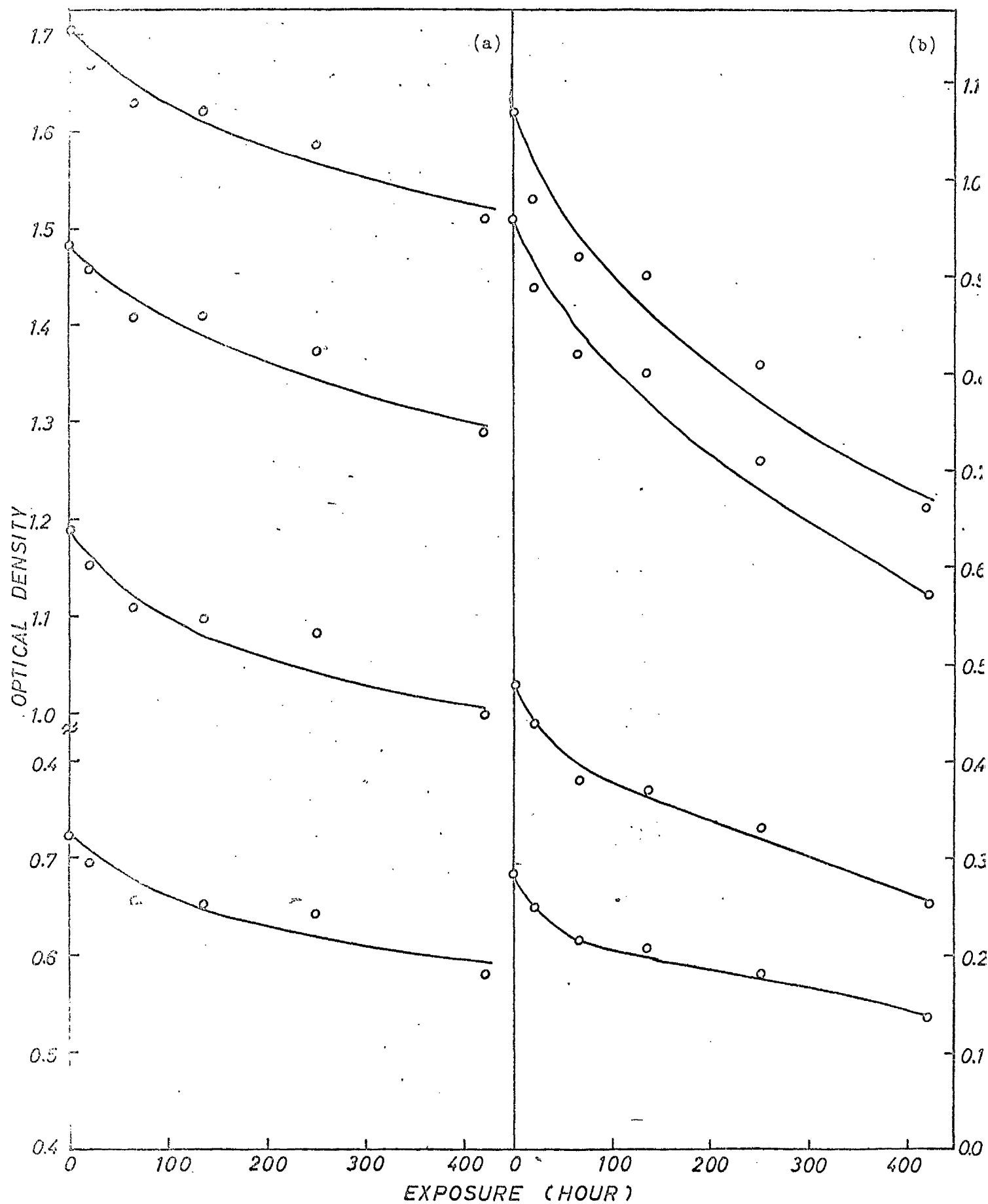


Fig. 48 Fading rate curves of Drimarene Discharge Orange X-3LG. on Cellophane.
 (a) Fixed.
 (b) Unfixed.

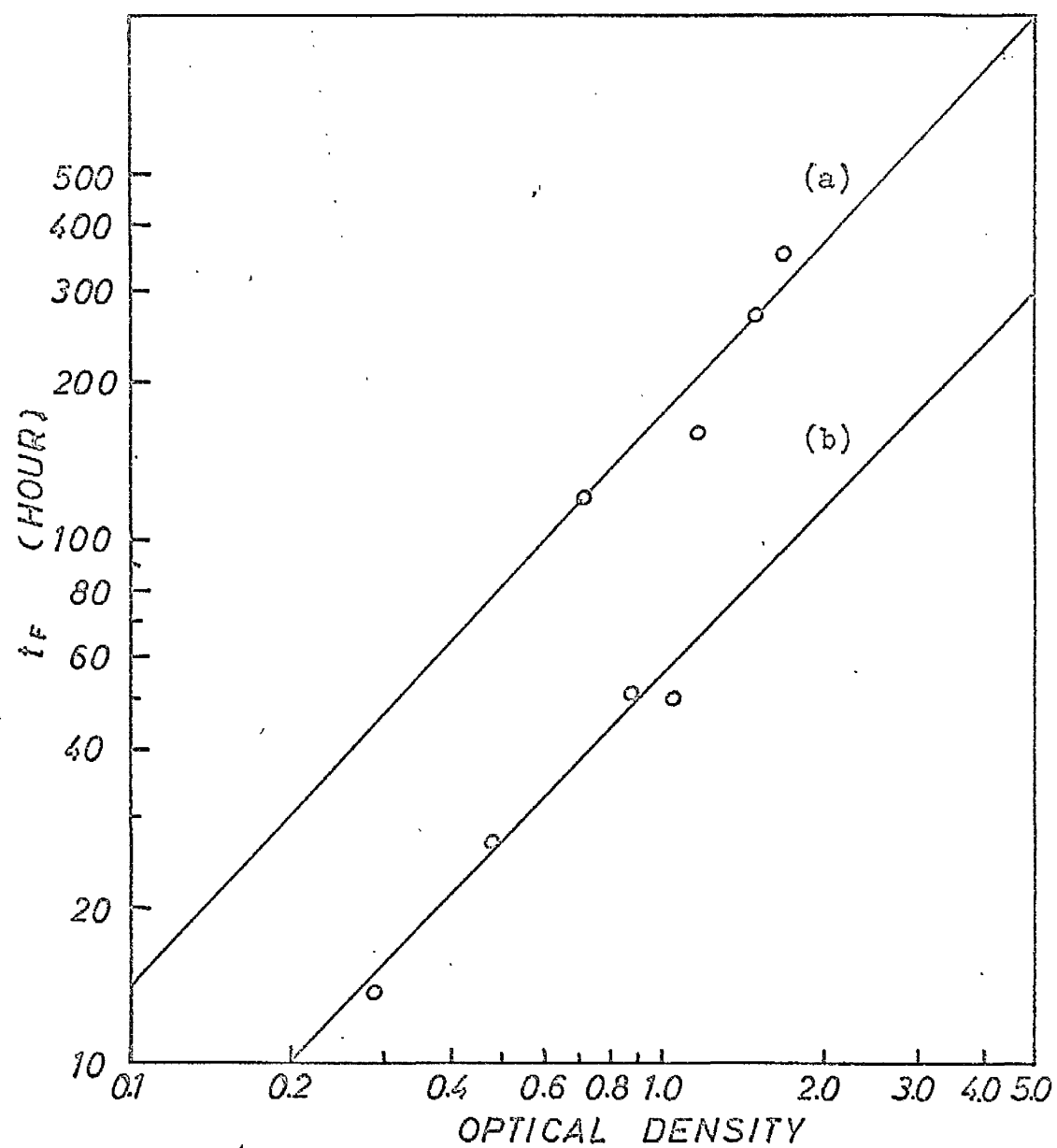
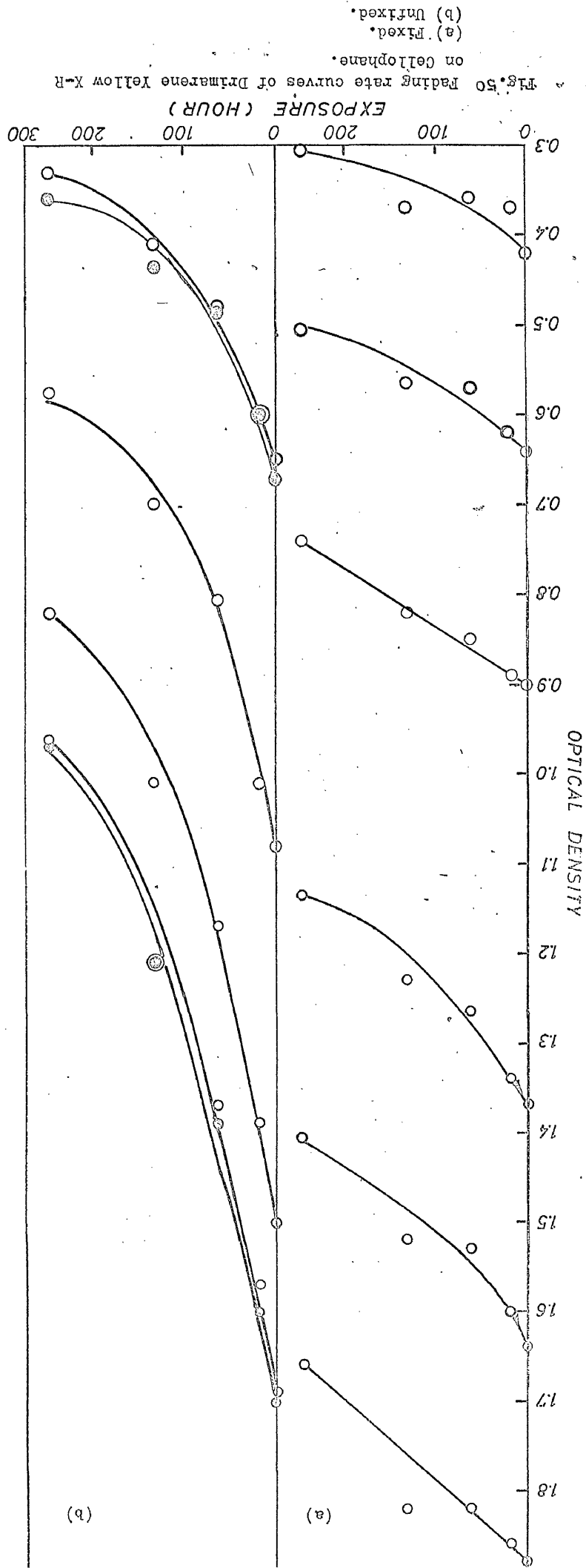


Fig. 4a CF curves of Drimarene Discharge Orange X-3LG on Cellophane.

(a) Fixed.

(b) Unfixed.



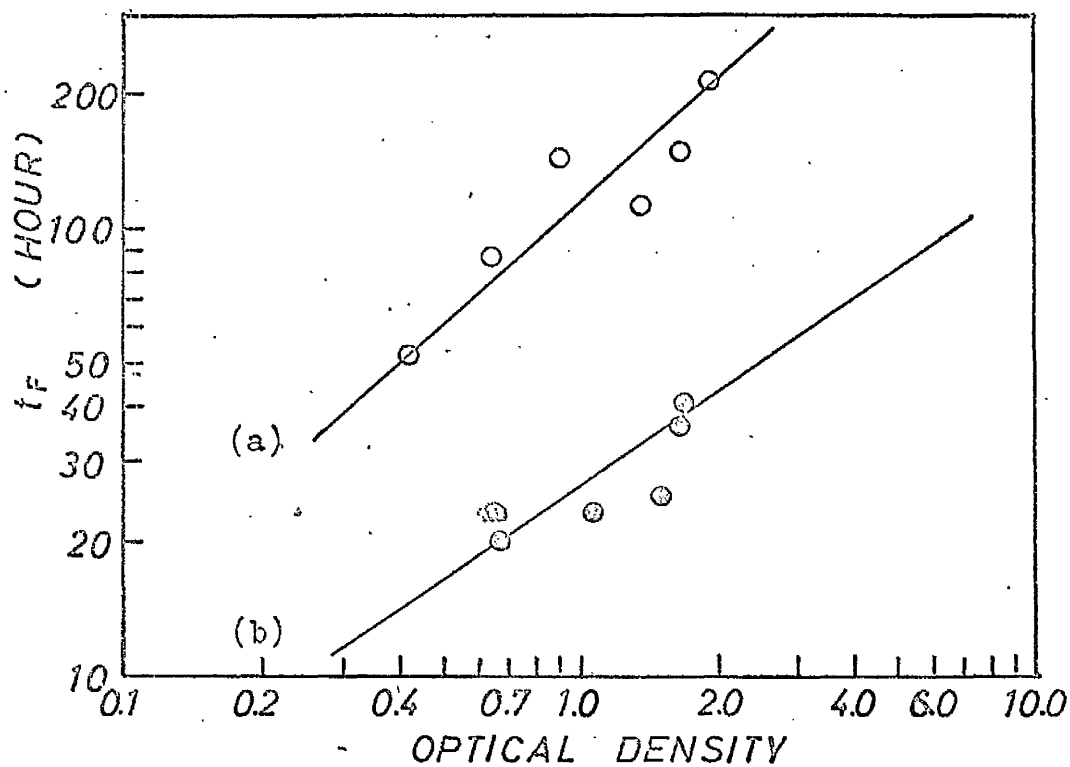


Fig. 51 CF curves of Drimarene Yellow X-R
on Cellophane.

- (a) Fixed.
- (b) Unfixed.

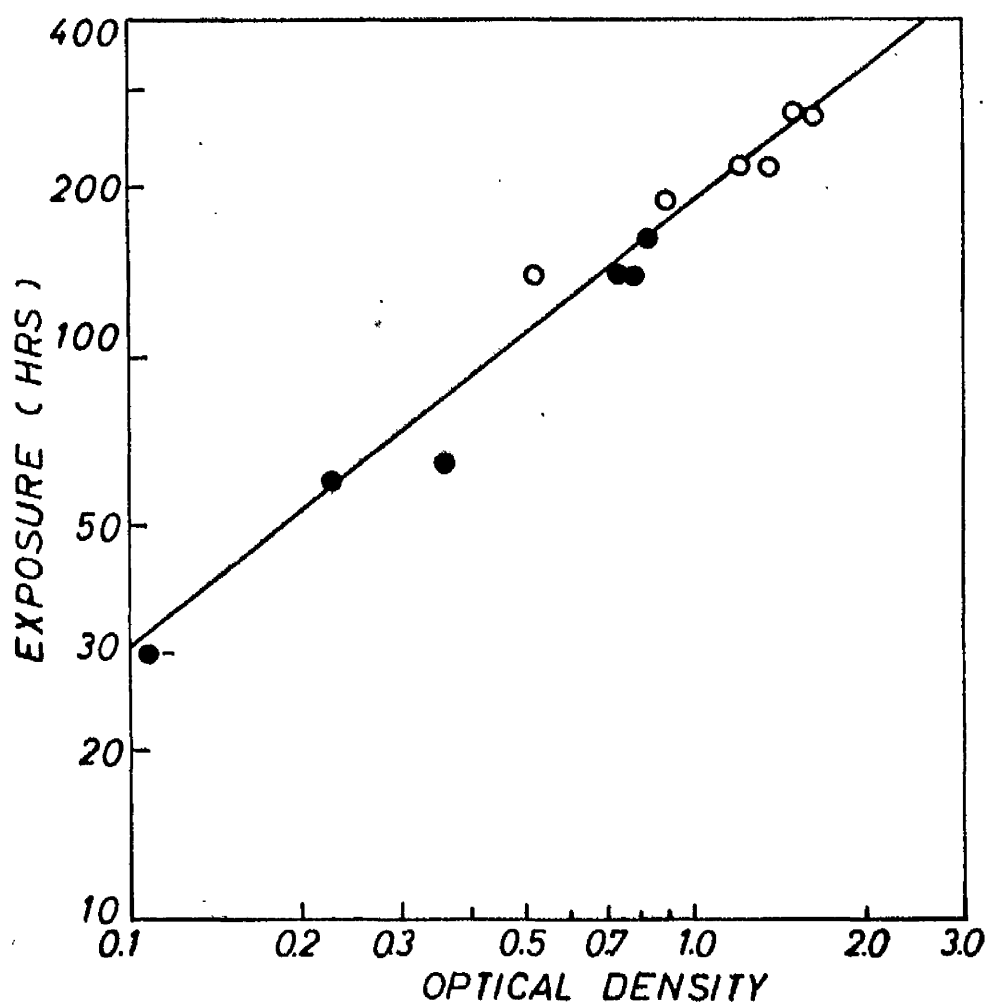


Fig. 52 CF curves of Remazol Red 3B on Cellophane.

- Fixed.
- Unfixed.

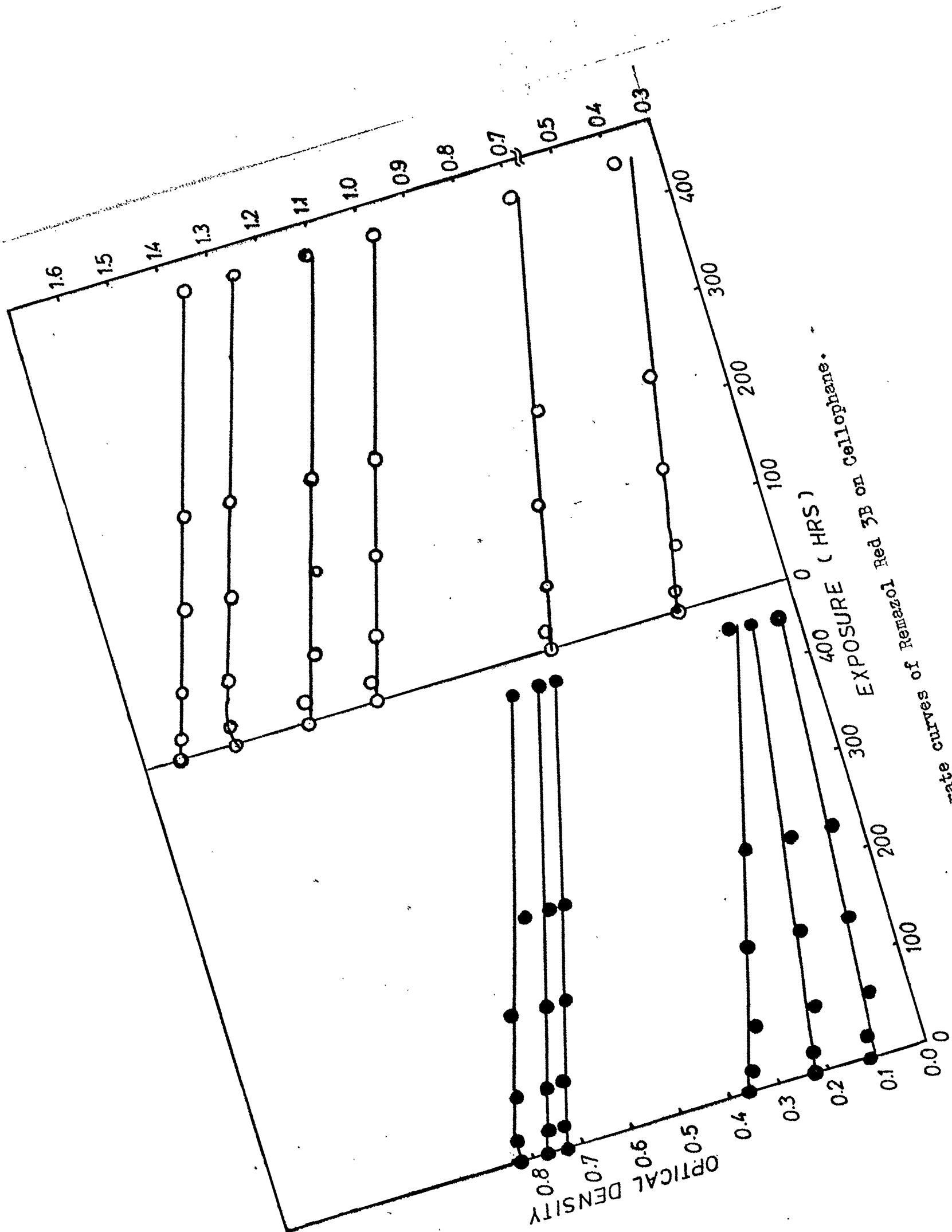


Fig. 53 Fading rate curves of Remazol Red 3B on Cellophane.
 O Fixed.
 • Unfixed.

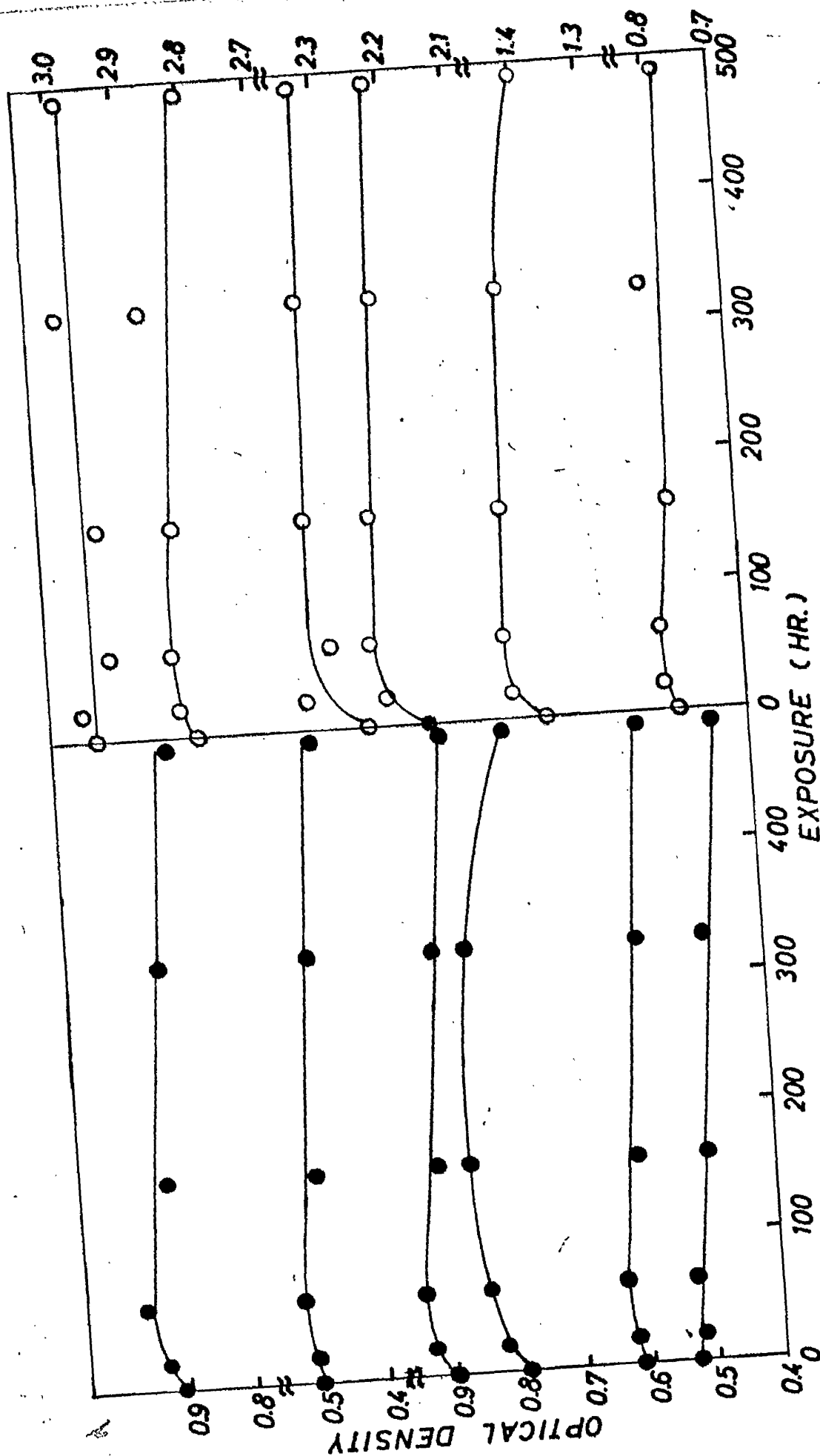


Fig. 54 Fading rate curves of Remazol Brilliant Blue R on Cellophane.

○ Fixed.
● Unfixed.

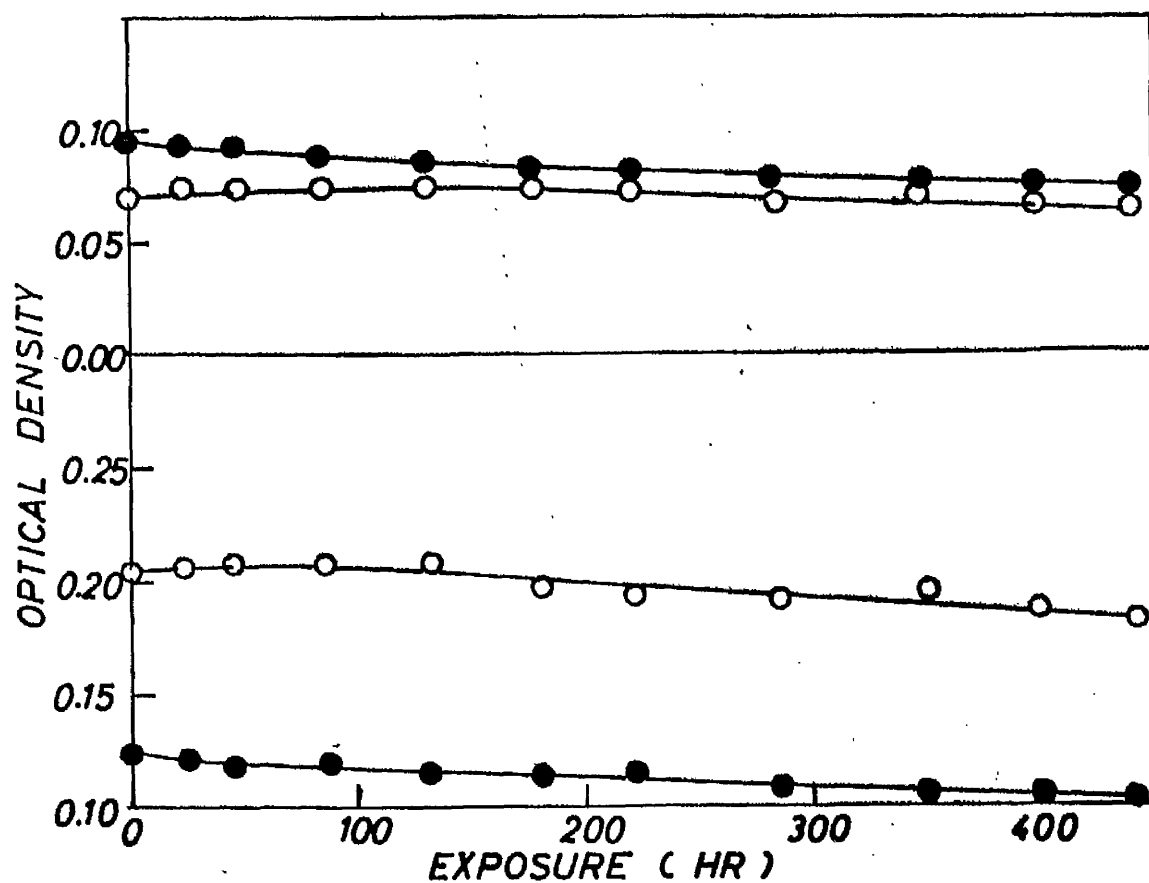


Fig.55 Fading rate curves of Remazol Red 3B on Cellophane.

- Fixed.
- Unfixed.

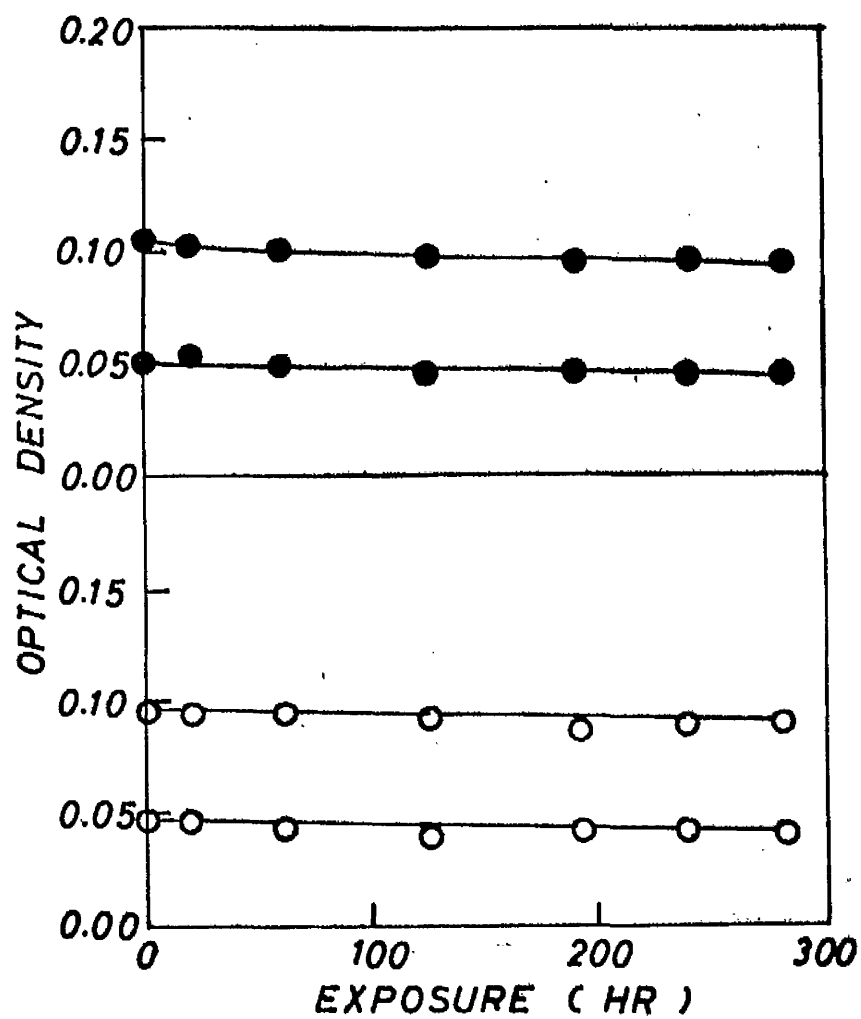


Fig. 56 Fading rate curves of Remazol Yellow RTN on Cellophane.

- Fixed.
● Unfixed.

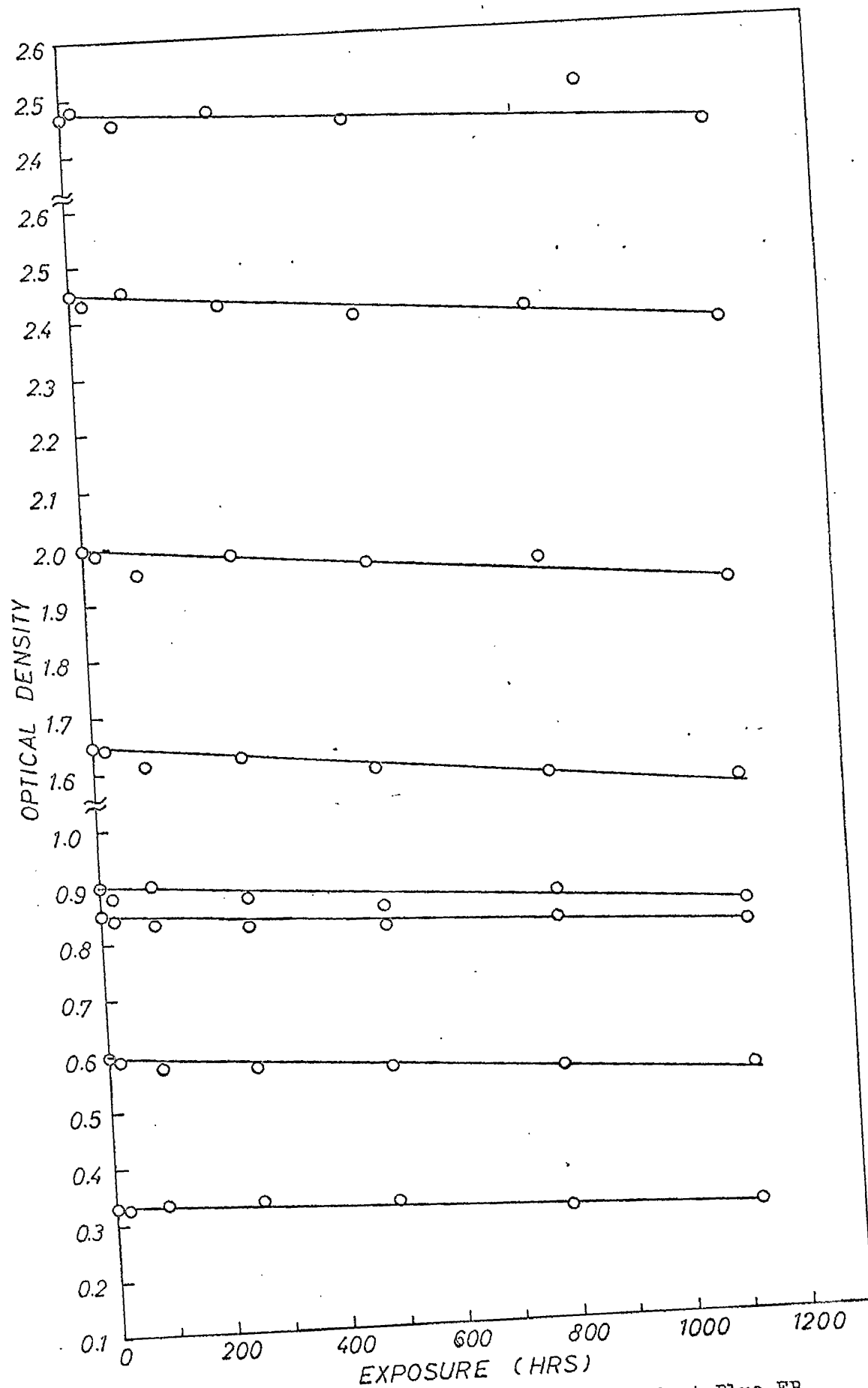


Fig.57 Fading rate curves of Levafix Brilliant Blue EB on Cellophane (all unfixed dyeings).

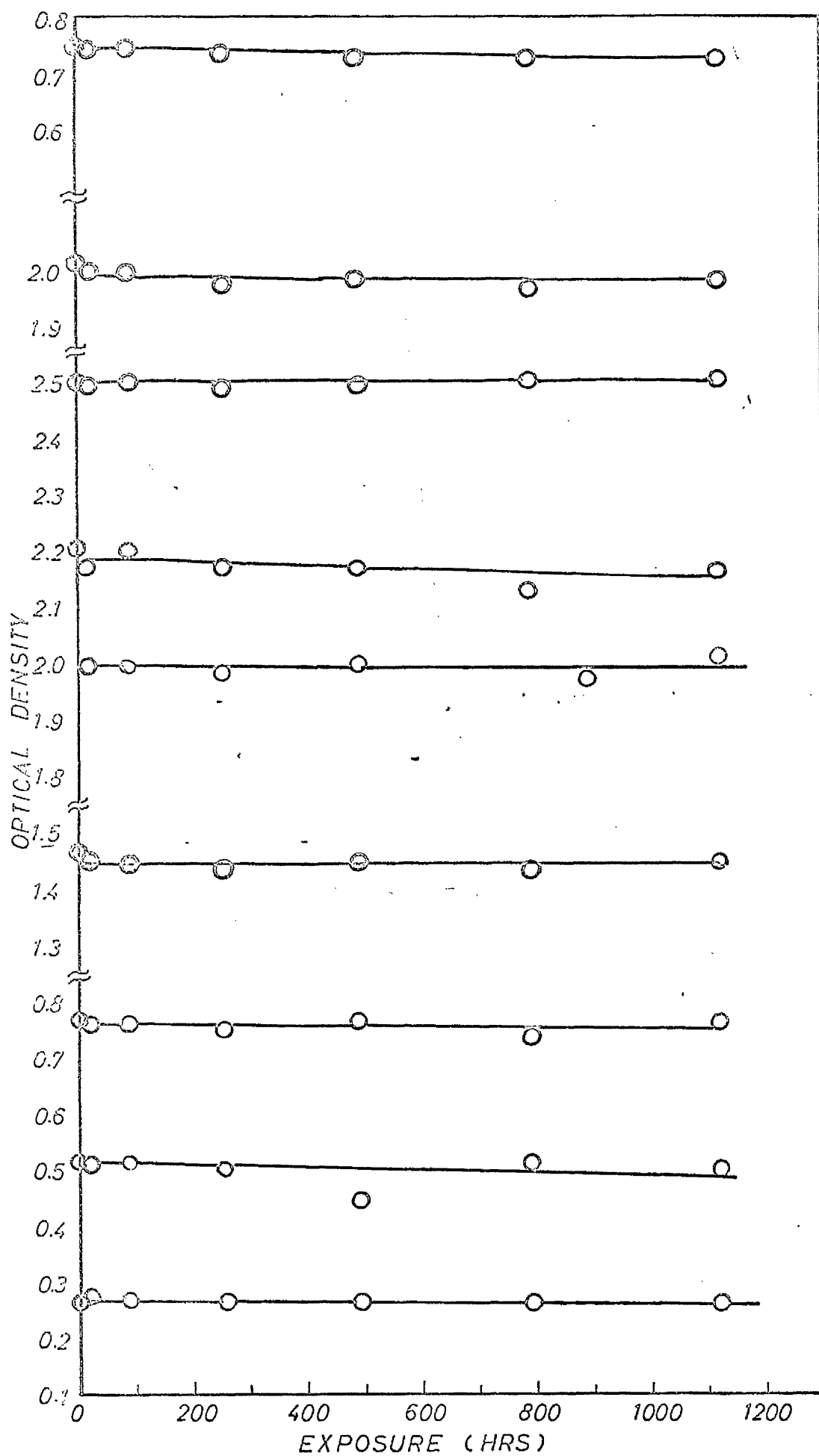


Fig.58 Fading rate curves of Levafix Brilliant Blue EB on Cellophane (all fixed dyeings).

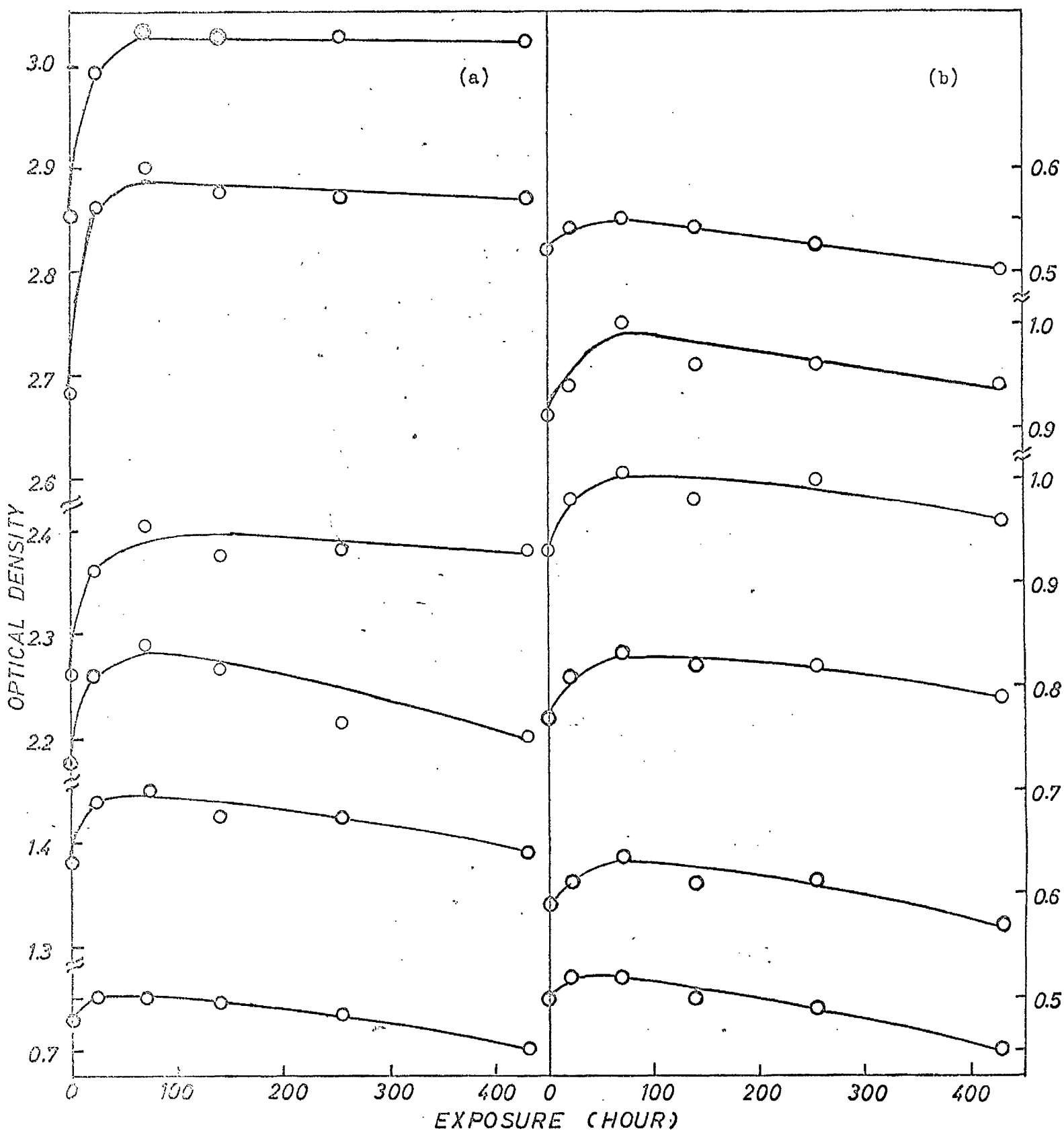


Fig. 59 Fading rate curves of Drimarene Turquoise X-G on Cellophane.

(a) Fixed.

(b) Unfixed.

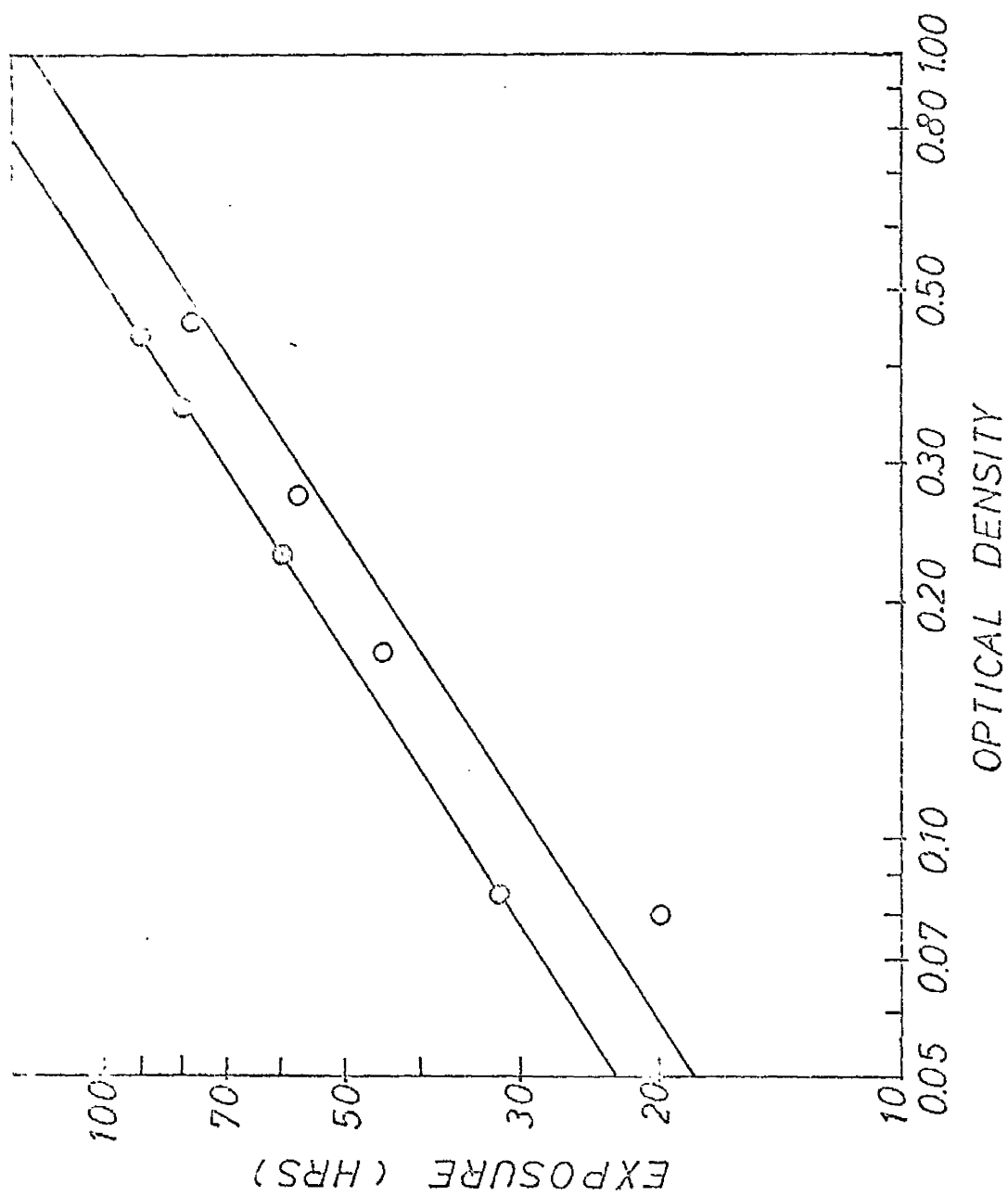


Fig. 60 CP curves of Procion Brilliant Orange G on Cellofas with glucose at pH 10.5 (○) and pH 5.6 (○). Fading recorded is 20%.

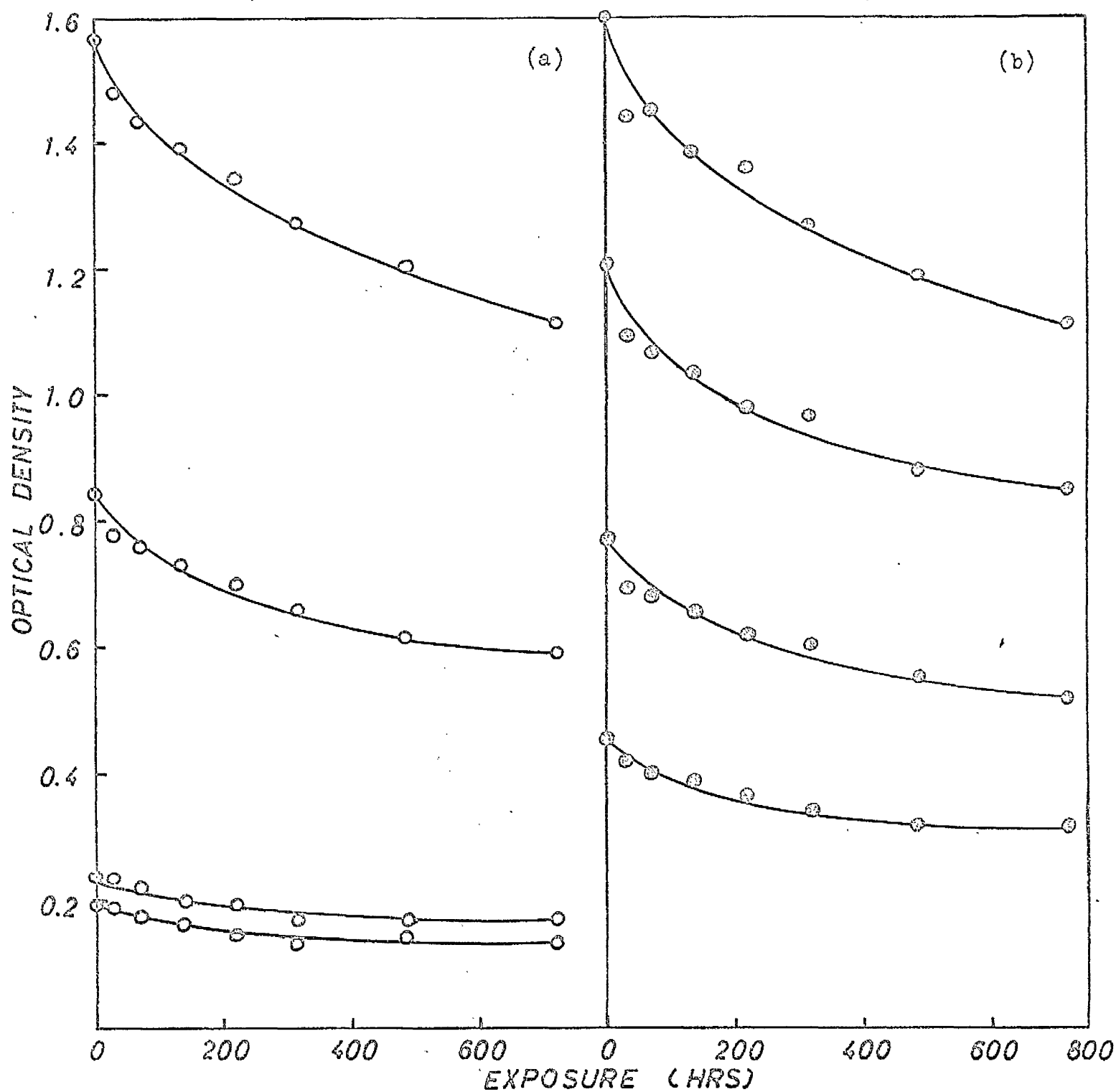


Fig. 61 Fading rate curves of Procion Brilliant Orange M - GS on Cellophane.

(a) Dye hydrolysed before dyeing (Unfixed dyeing).

(b) Unhydrolysed dye (Fixed dyeing)

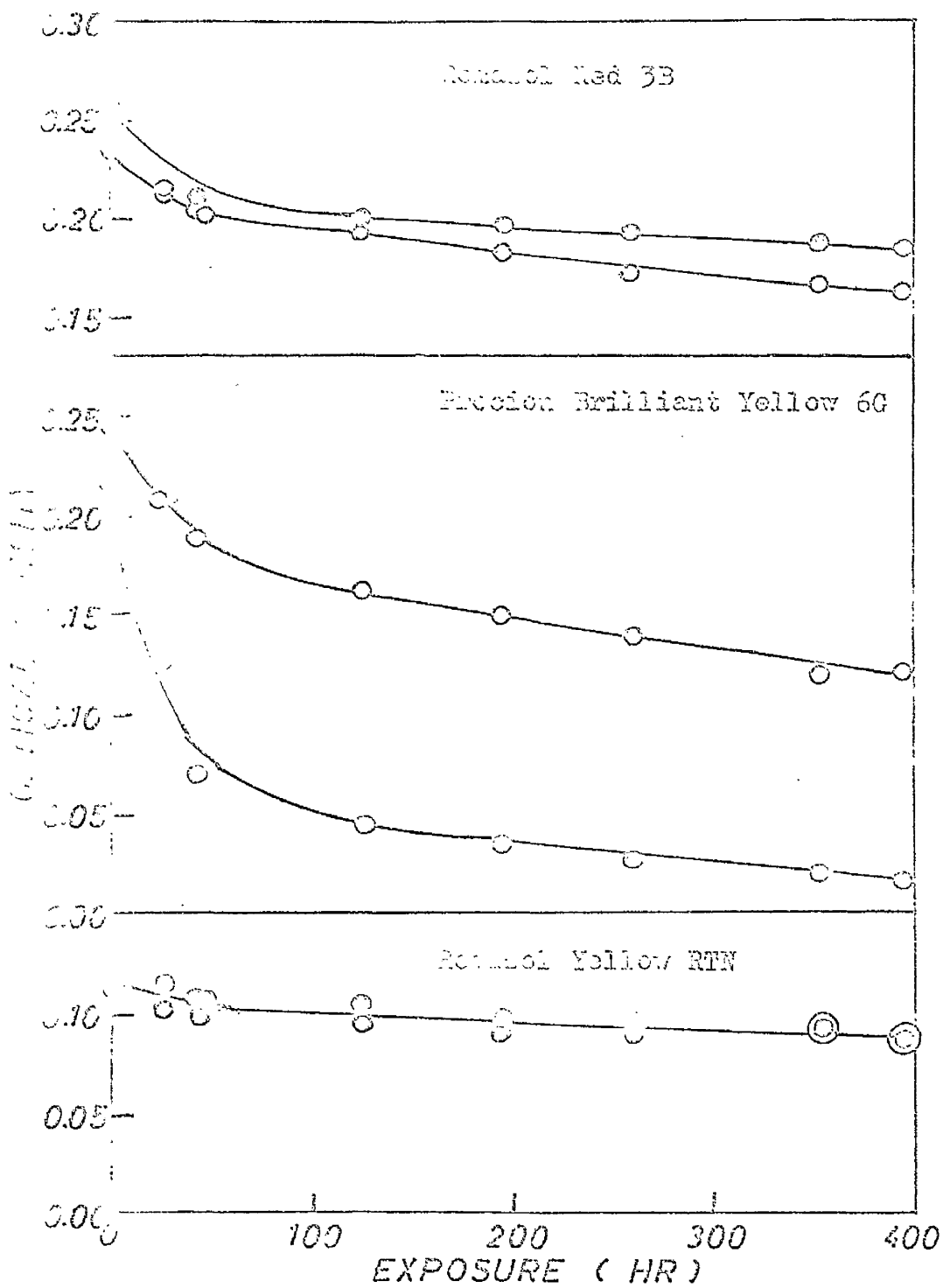


Fig. 62 Fading of hydrolysed and unhydrolysed dye.

- Hydrolysed.
- Unhydrolysed.

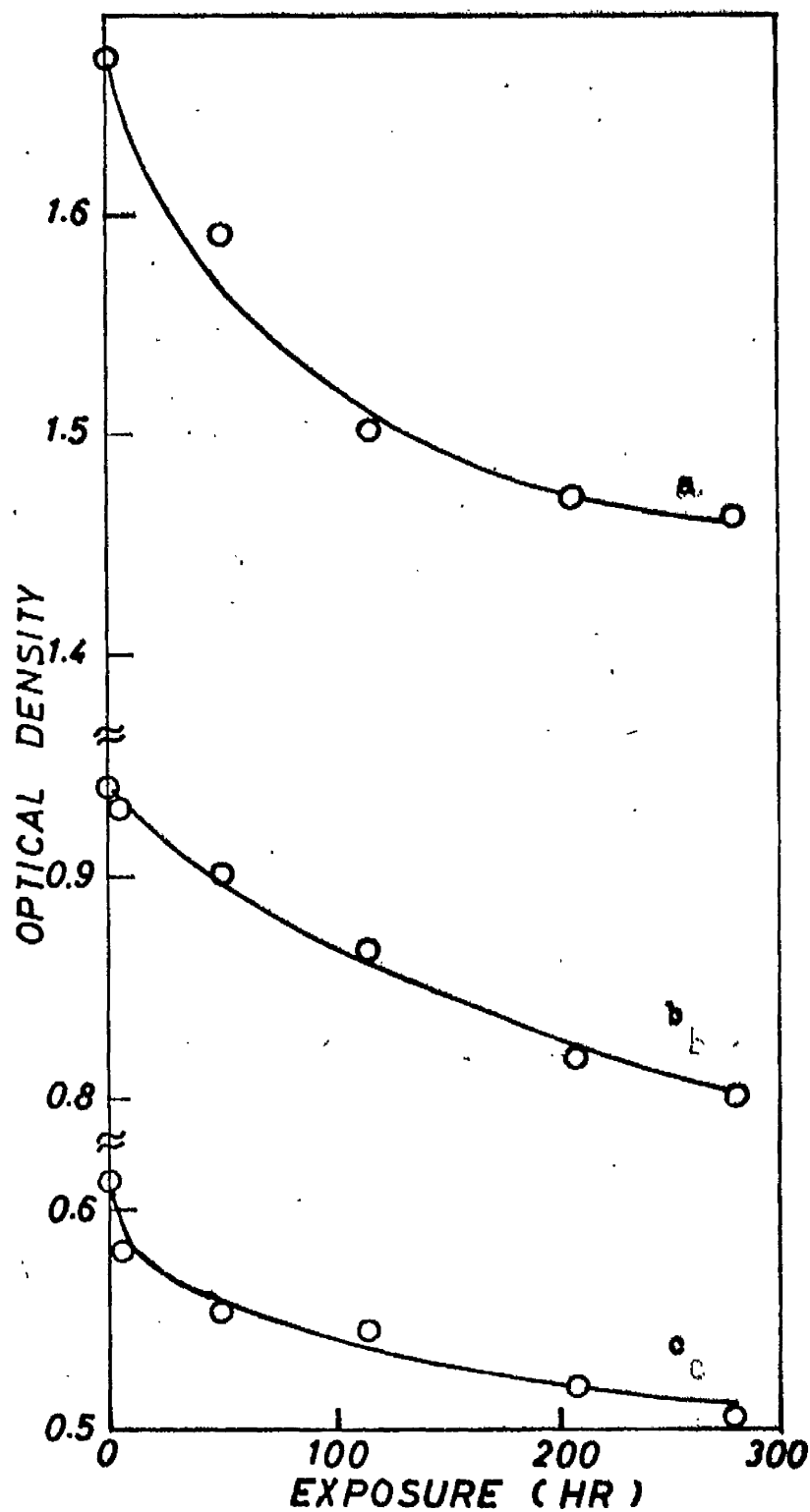


Fig. 63 Fading of Cibacron Scarlet 2G.

- (a) Unfixed.
- (b) Fixed.
- (c) Treated with methanol.

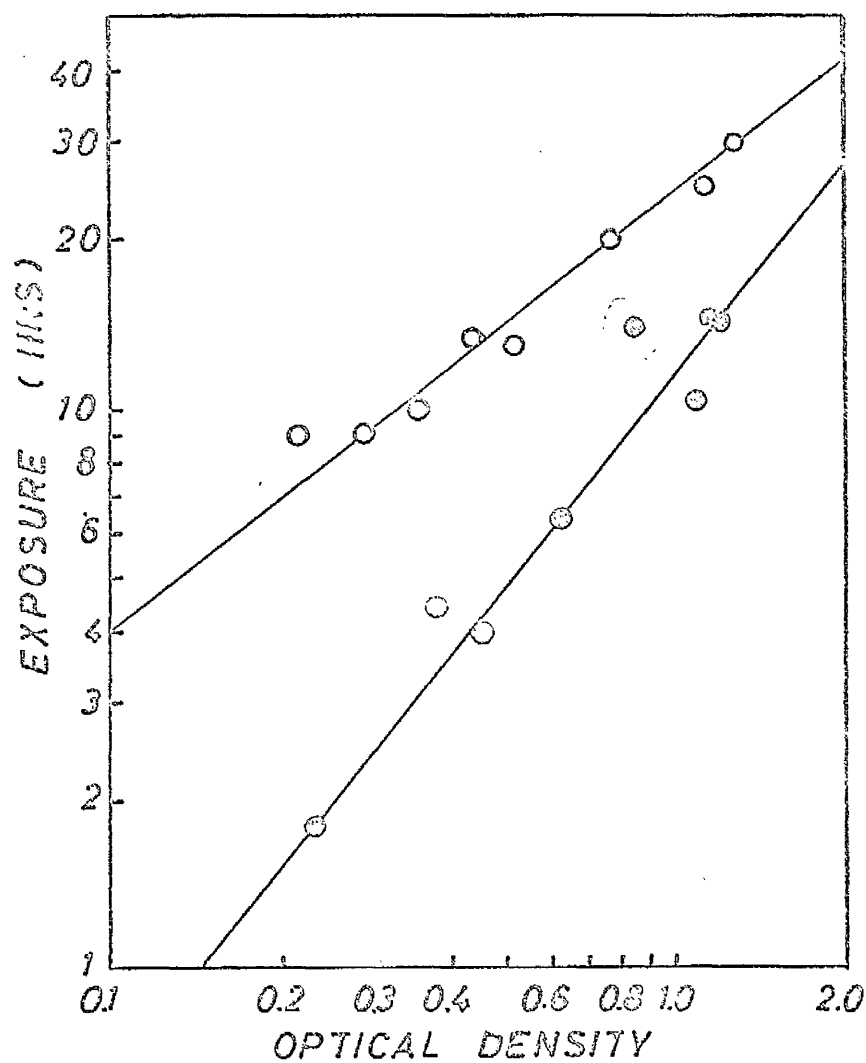


Fig. 64 CF curves of Direct Pink G on Cellophane.

- Fixed.
- ⊙ Unfixed.

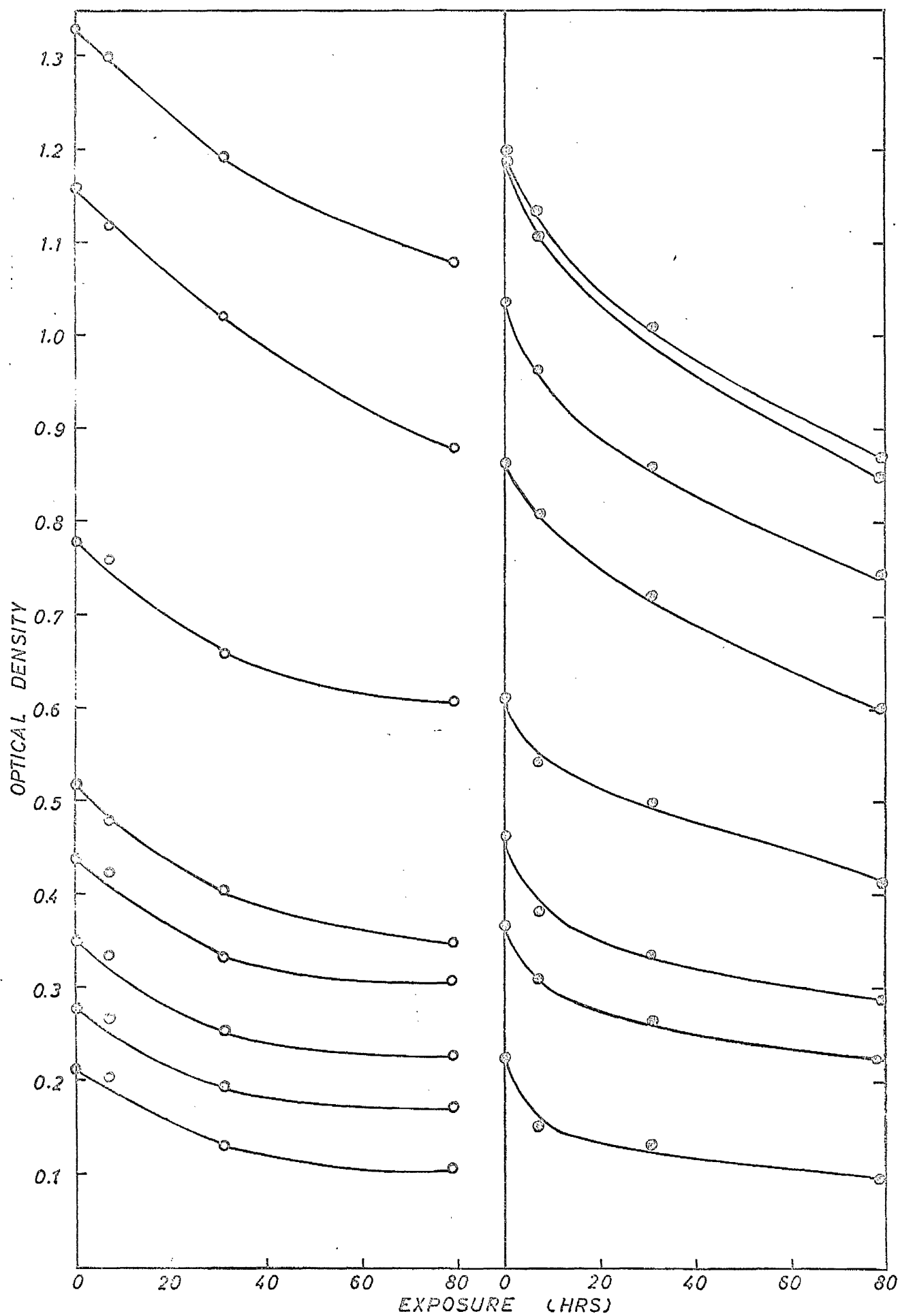


Fig. 65 Fading of Direct Pink G on Cellophane. O Fixed; ● Unfixed.

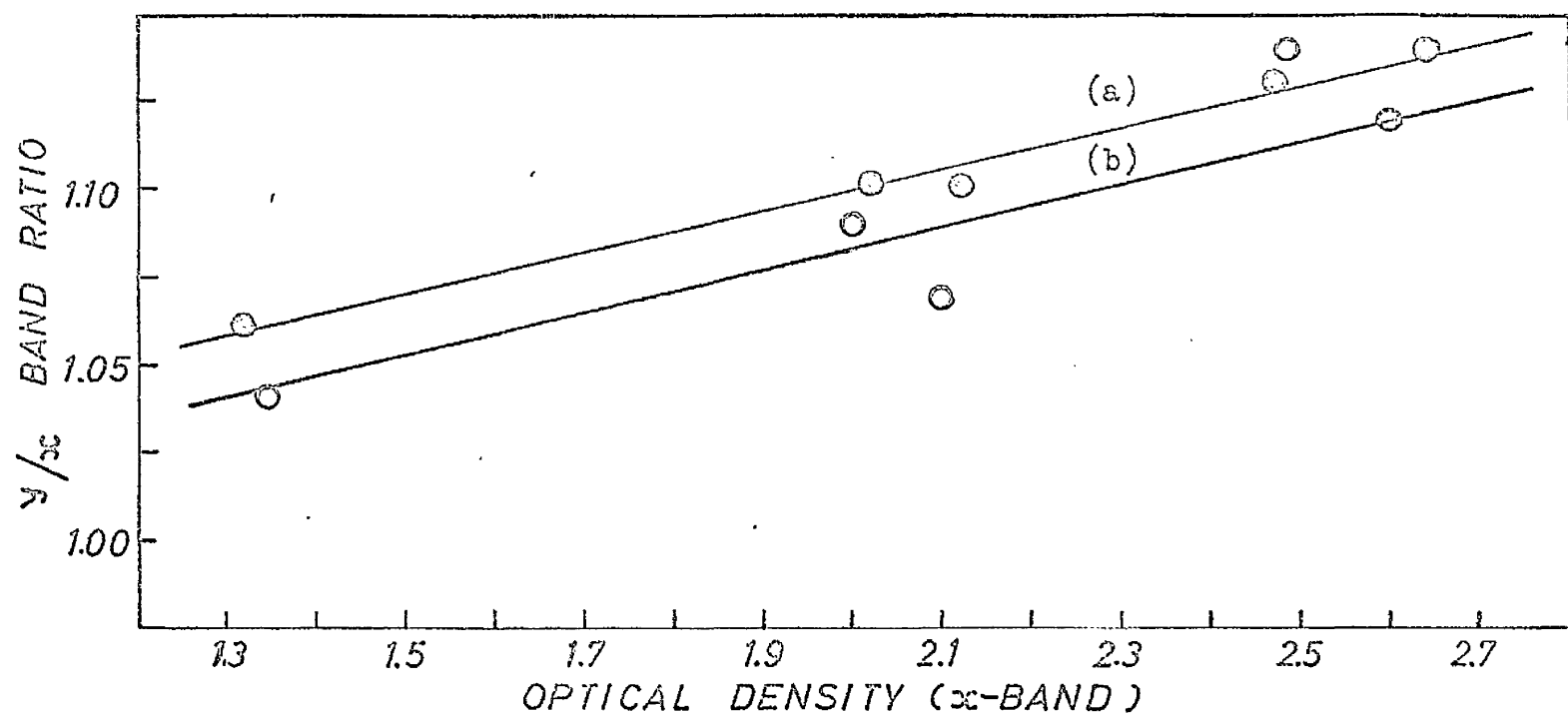


Fig. 66 y/x to x band ratio before and after fading of fixed dyeings of Remazol Brilliant Blue R.

(a) After fading.

(b) Before fading.

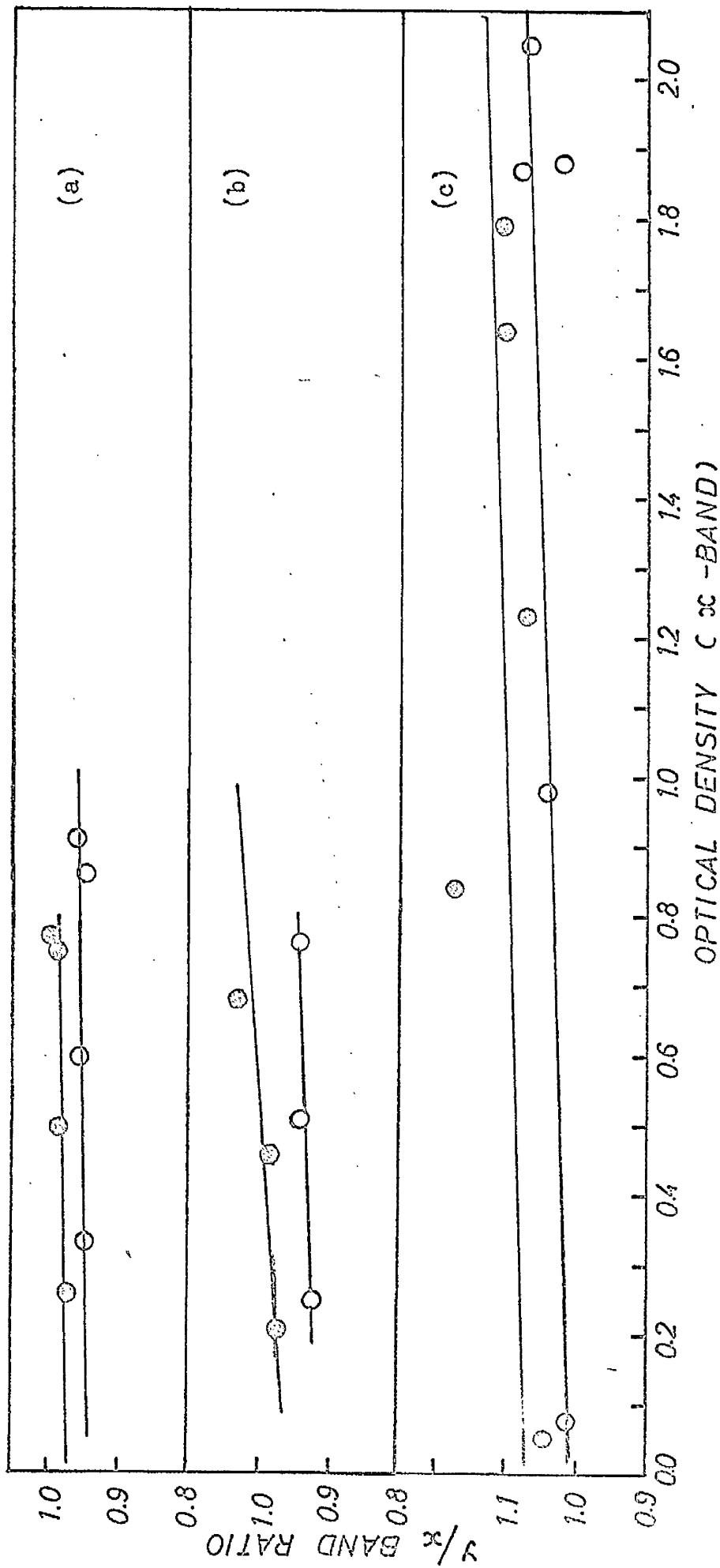


Fig. 67 y/x to x band ratio before and after fading of (a) Levafix Brilliant Blue EB (unfixed), and (b) Levafix Brilliant Blue EB (fixed), and (c) Procion Brilliant Orange M-GS (fixed).

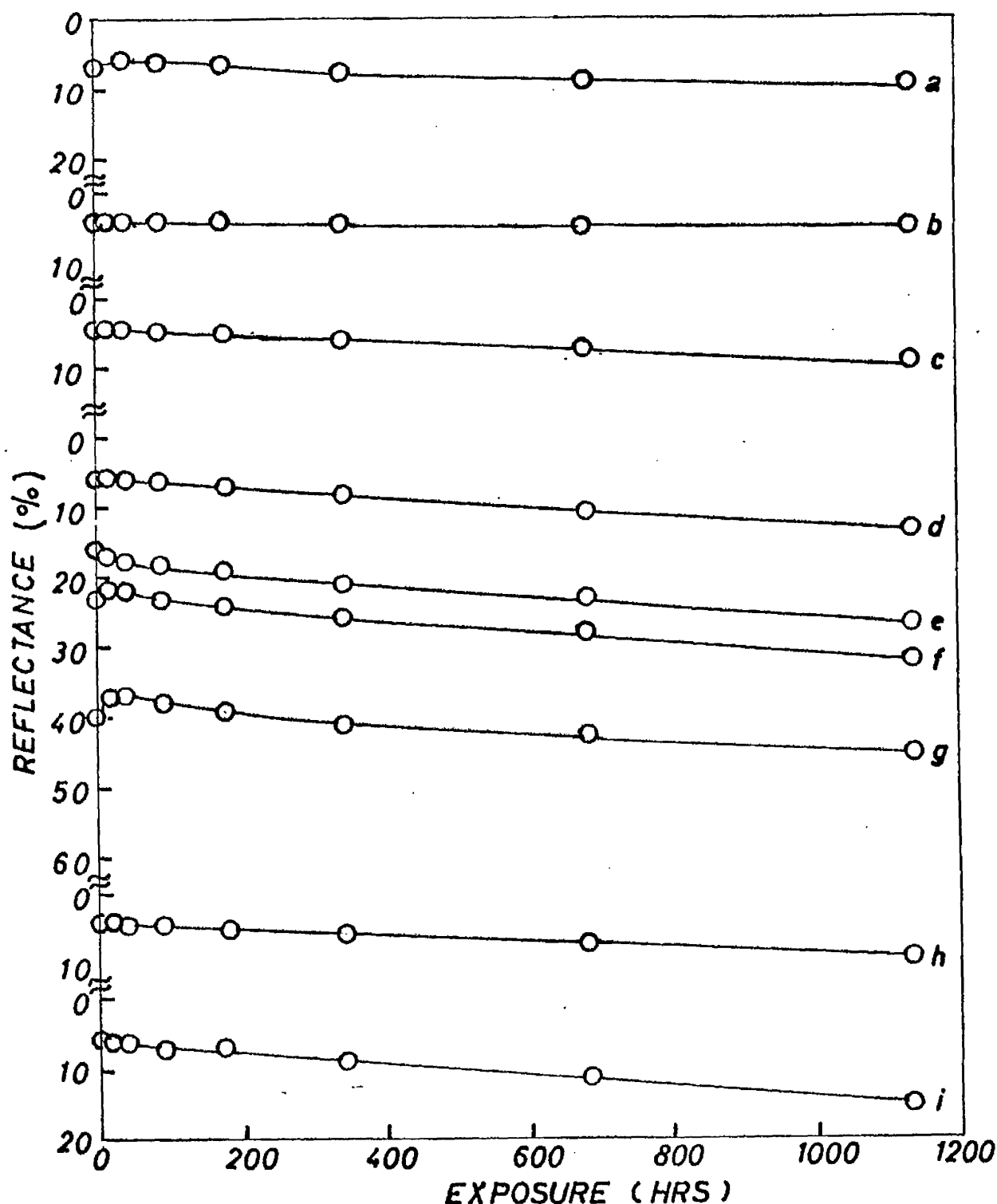


Fig. 68 Fading of Levafix Brilliant Blue EB on poplin by reflection measurements. (a) Shade 15g/l with urea and sodium carbonate, and soaped; (b) 30 g/l, and (c) 45 g/l ; rest same as in (a); (d) 30 g/l without urea and sodium carbonate, washed with cold water; (e) 45 g/l without urea and sodium carbonate, and unwashed; (f) same as (e) but washed with cold water; (g) 15 g/l without urea and sodium carbonate, and washed with cold water; (h) same as (g) but unwashed; (i) 30 g/l with half urea and half sodium carbonate, and soaped.

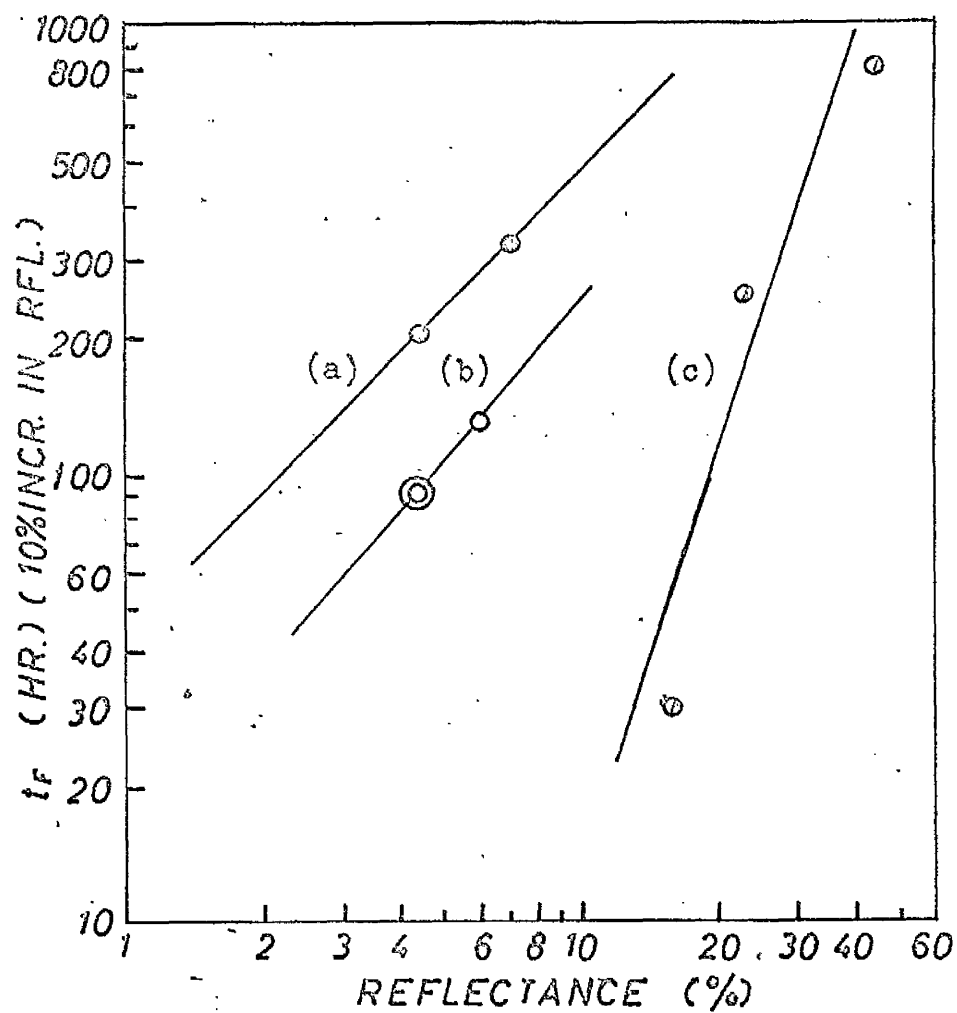
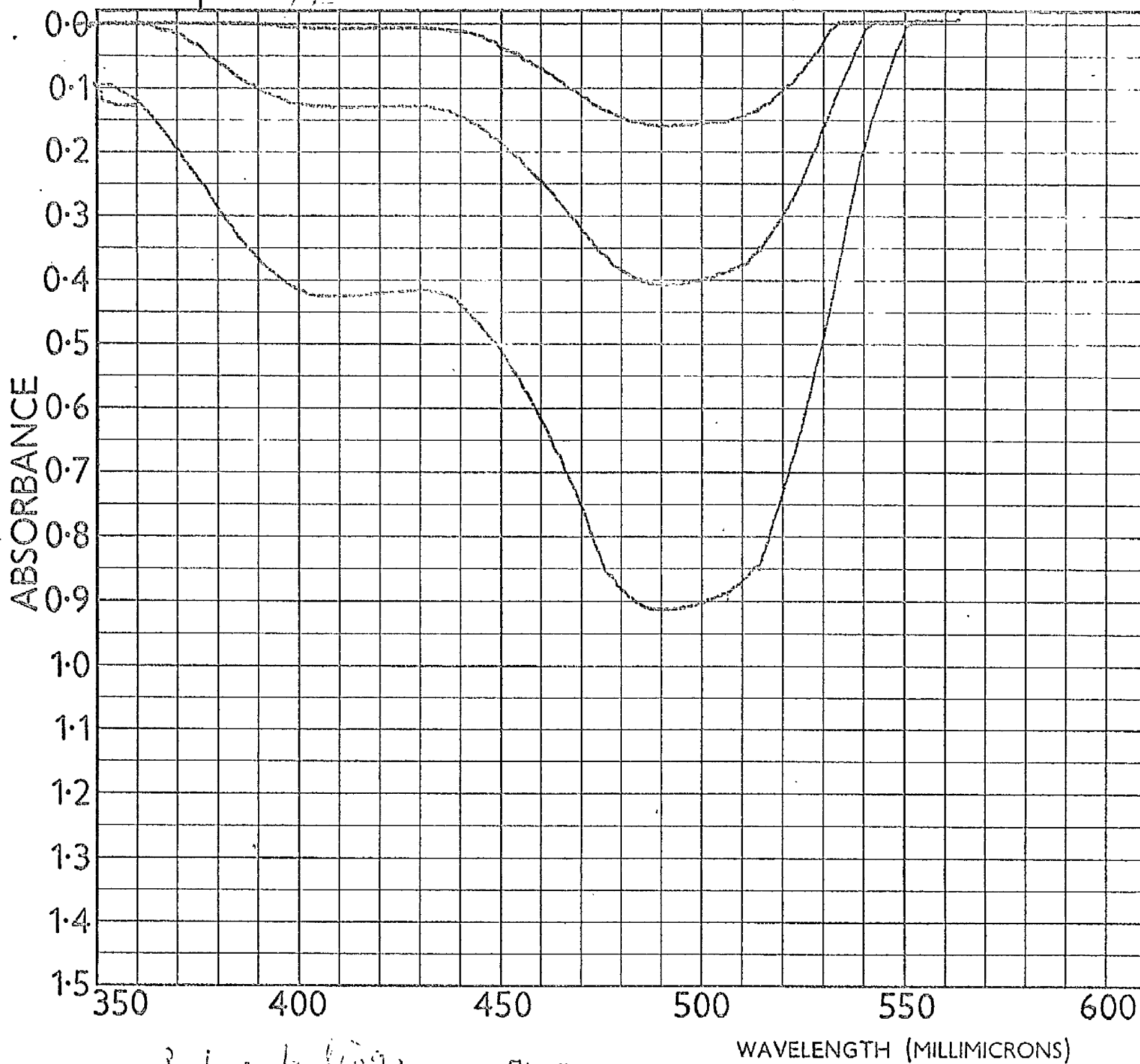


Fig. 69 CF curves of Levafix Brilliant Blue EB on Poplin.

(a) Unfixed and unwashed.

(b) Unfixed and washed cold.

(c) Fixed and soaped.



Before fading

Fig. 70

SAMPLE Int. Brill. Orange MS 65

Five a Dyeings

ORIGIN _____

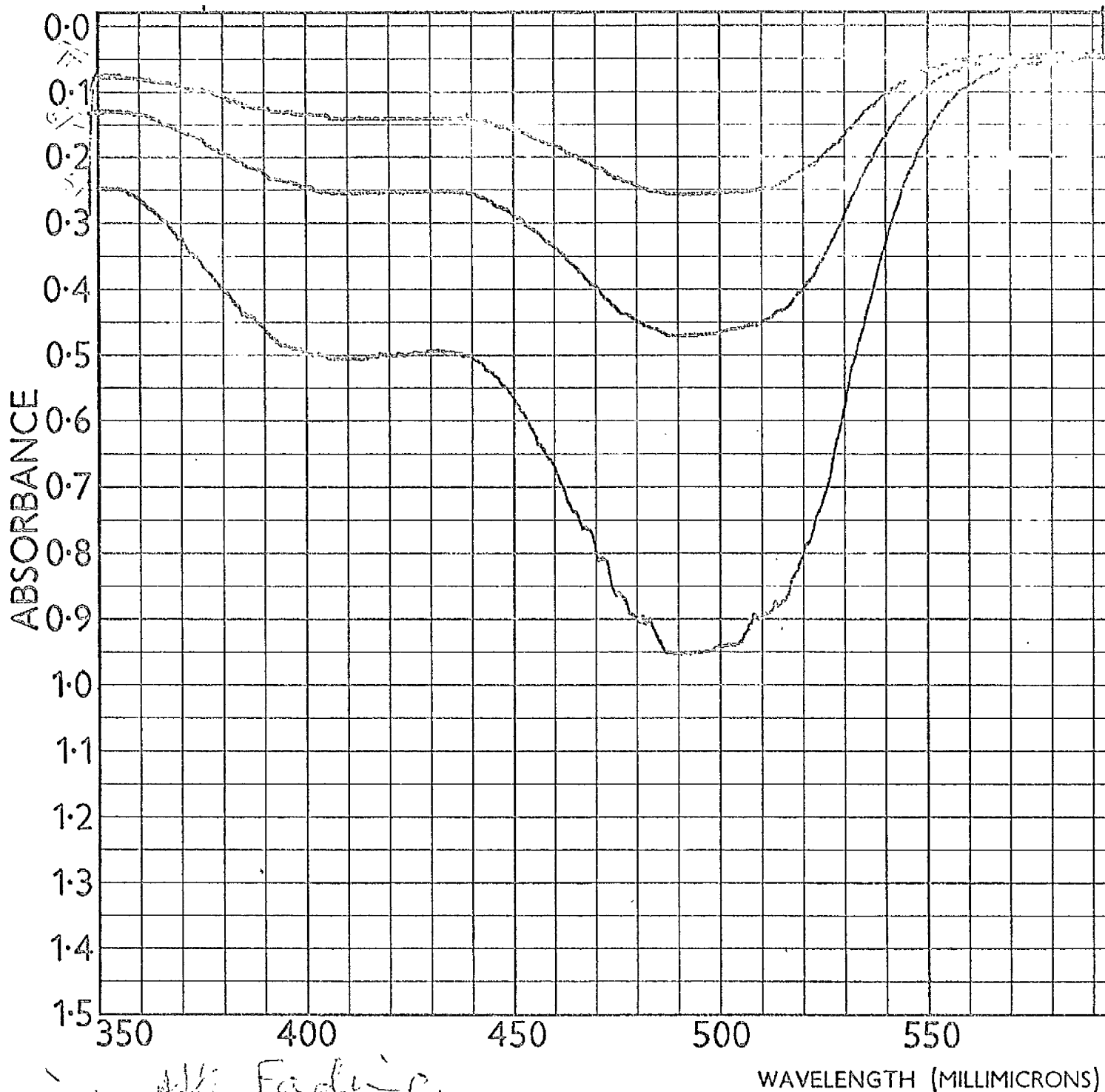
SOLVENT _____

CURVE NO _____

CONC _____

CELL PATH _____

REFERENCE _____

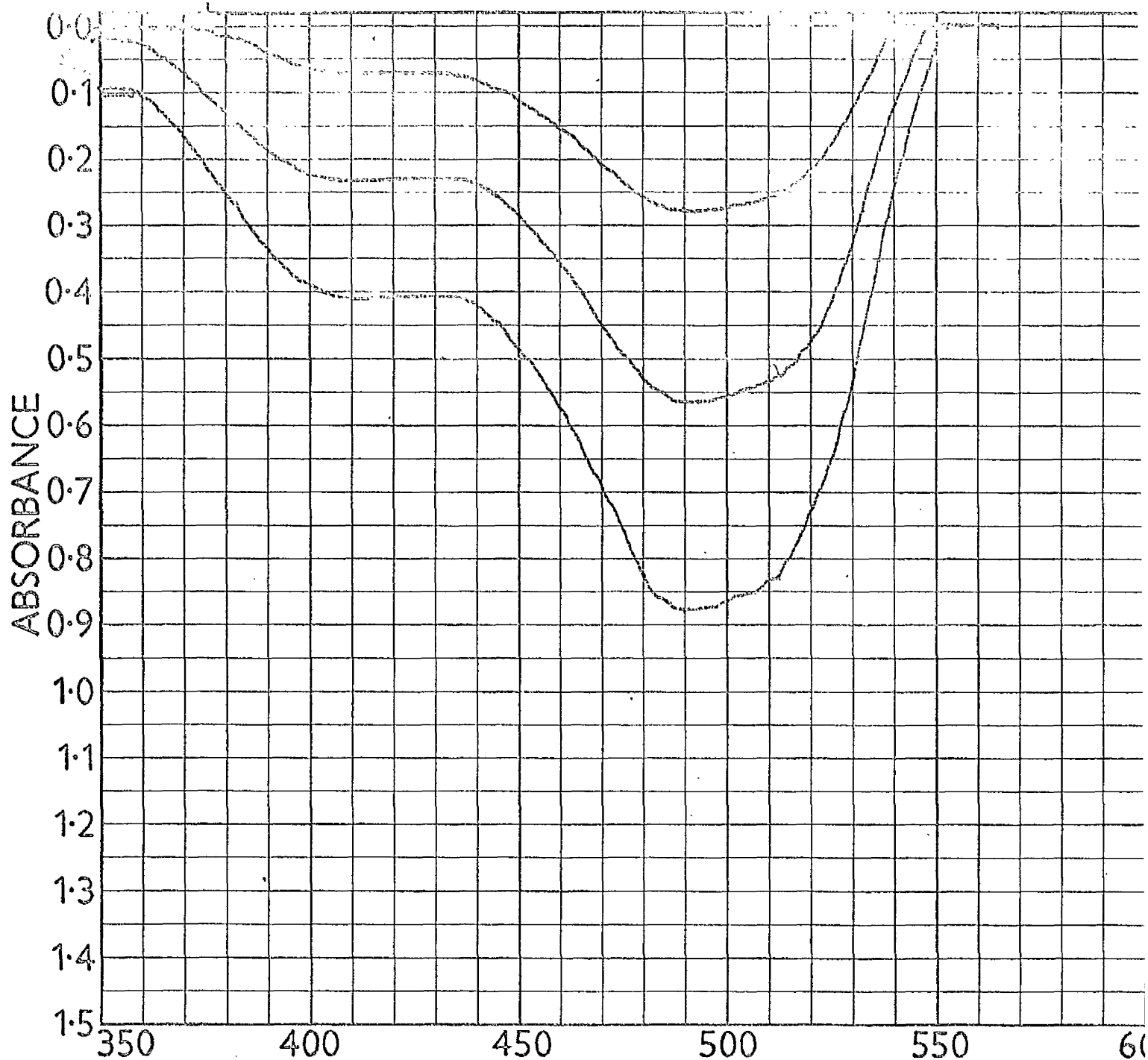


Alk. Faden p.

Fig. 71

SAMPLE Ac. Brill. Orange 5/5.
Fixed Dyeing
 ORIGIN E. Ingstedt as 27/4/65
 SOLVENT _____

CURVE NO _____
 CONC _____
 CELL PATH _____
 REFERENCE _____

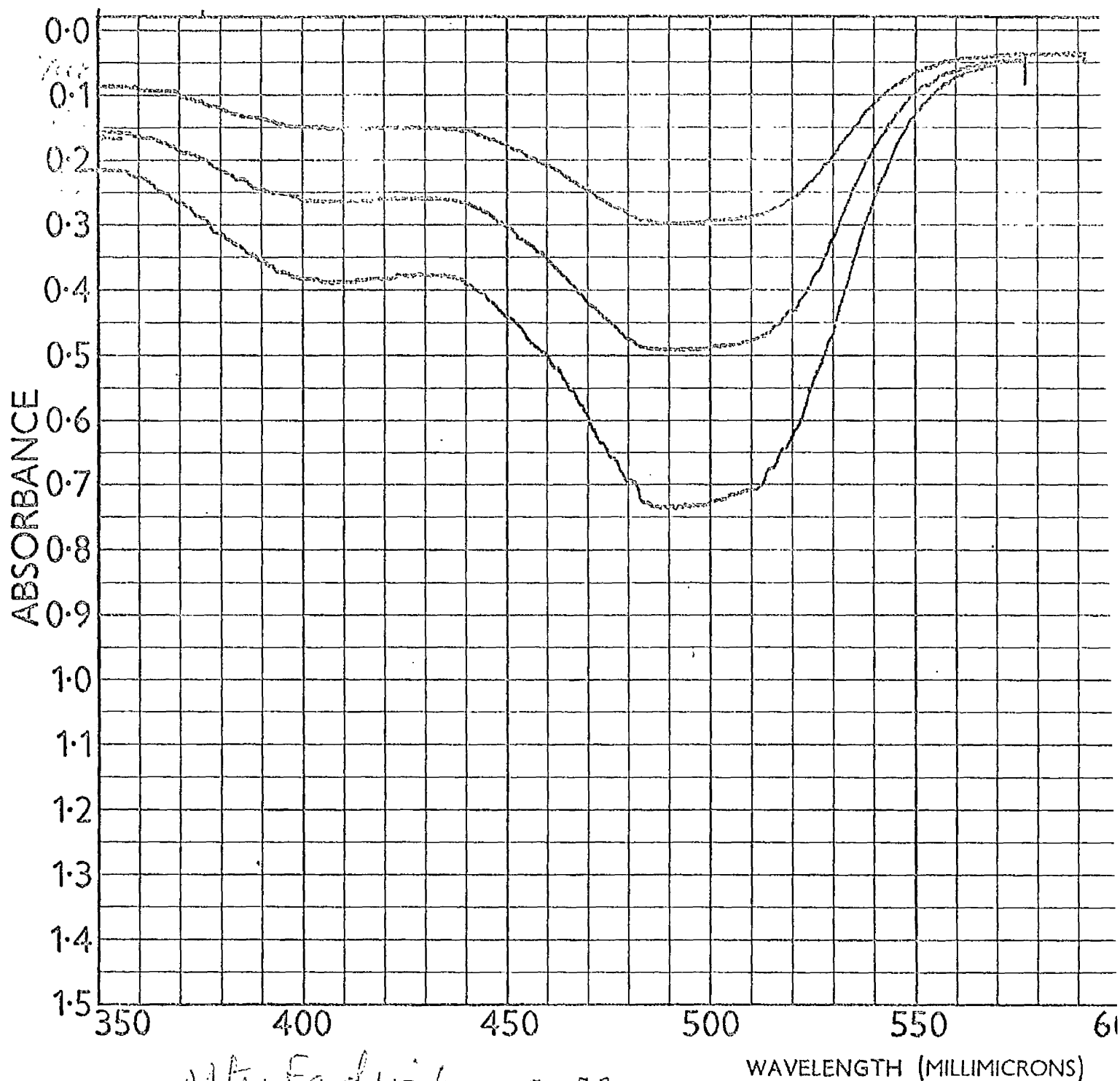


Before fading.

Fig. 72

WAVELENGTH (MILLIMICRONS)

SAMPLE <u>Pure, Brill. Orange MR 5.</u>	CURVE NO. _____
<u>Uniform dispersion</u>	CONC. _____
ORIGIN _____	CELL PATH _____
SOLVENT _____	REFERENCE _____



After Fading

Fig. 73

SAMPLE <u>Brown Brill. Orange 56</u>	CURVE NO _____
<u>Unfaded solution</u>	CONC _____
ORIGIN <u>Lab. Stock on 22/4/65</u>	CELL PATH _____
SOLVENT _____	REFERENCE _____

500

0.0

0.1

0.2

0.3

0.4

0.5

0.6

0.7

0.8

0.9

1.0

300

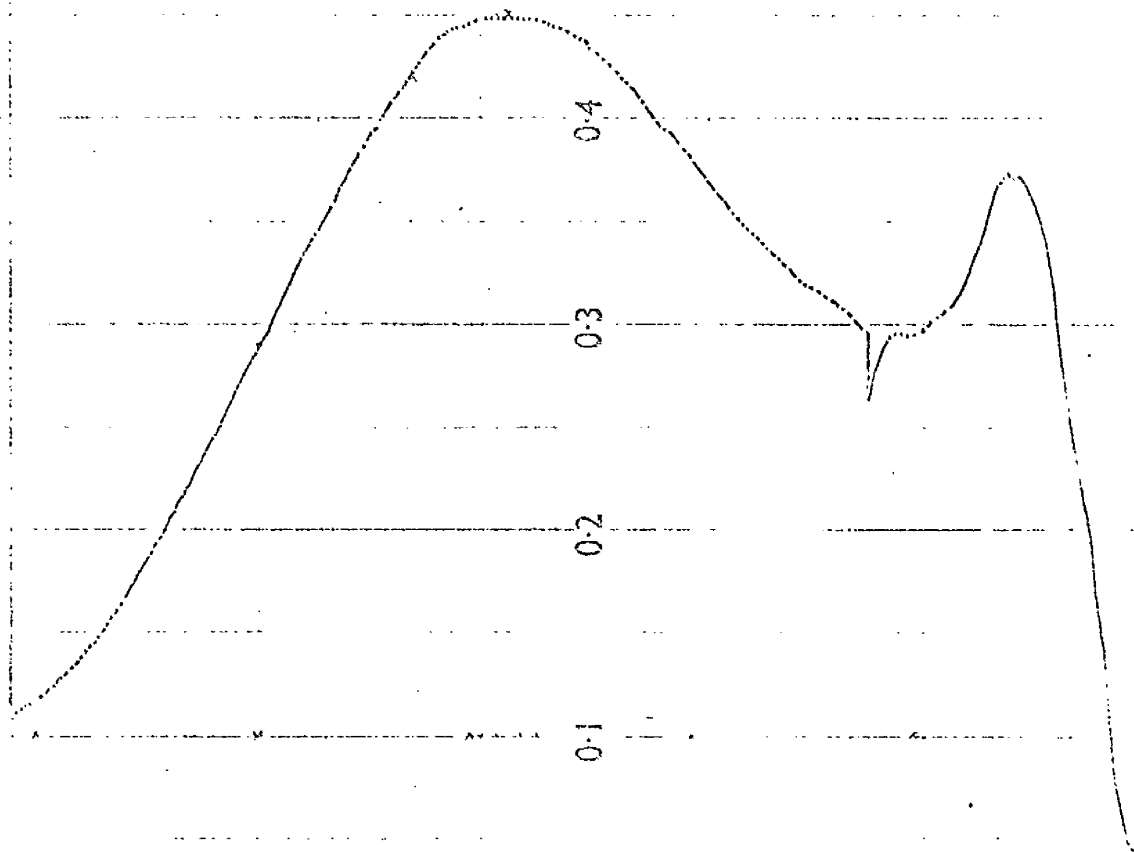
Fig. 74

(Pre-Built, yellow 66)

4 MF

Refractive Fading

SPECTRUM CUR
IN OPTIKA



500

0.1 0.2 0.3 0.4 0.5 0.6 0.7 0.8 0.9 1.0

500

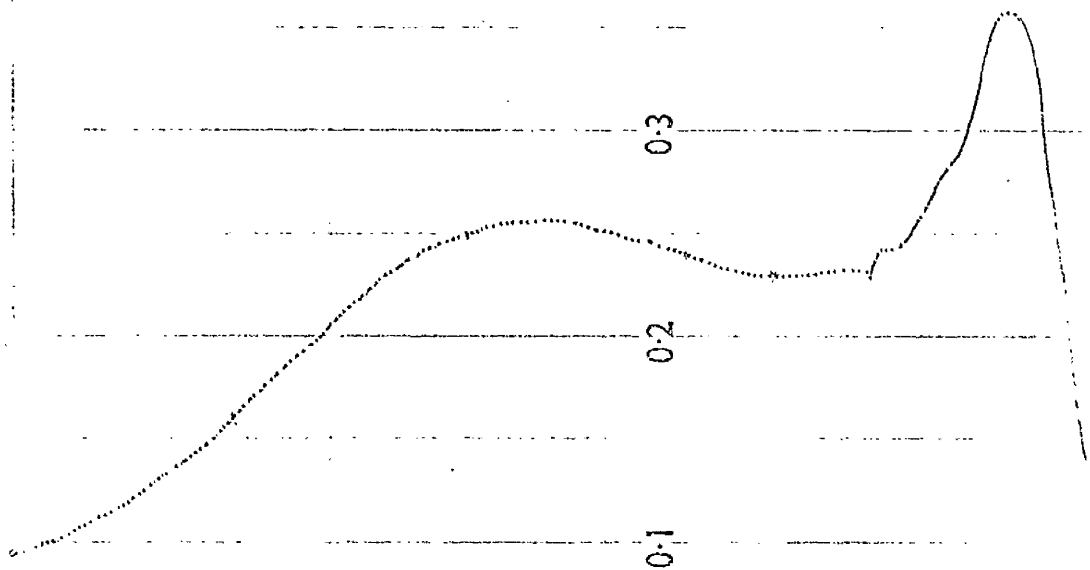
4uF₂

Fig. 75

(Proc. Bull. yellow 66)

4uF₂ After Fading

SPECTRUM CURVE



500

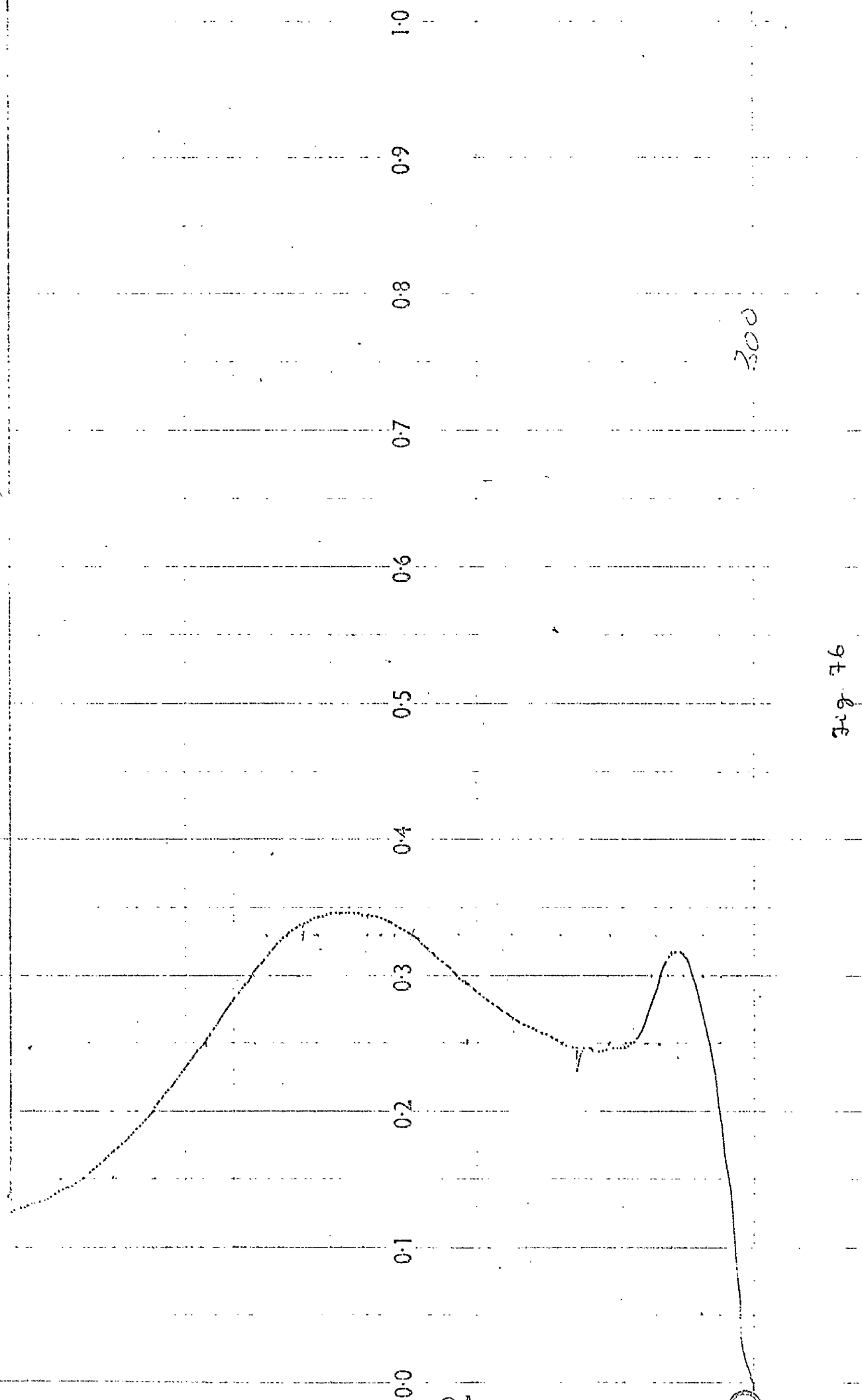


Fig. 76

SPECTRUM CURVE
ON OPTIKA

IF2 Before Fading

(Pre. Brill. yellow 665)

66

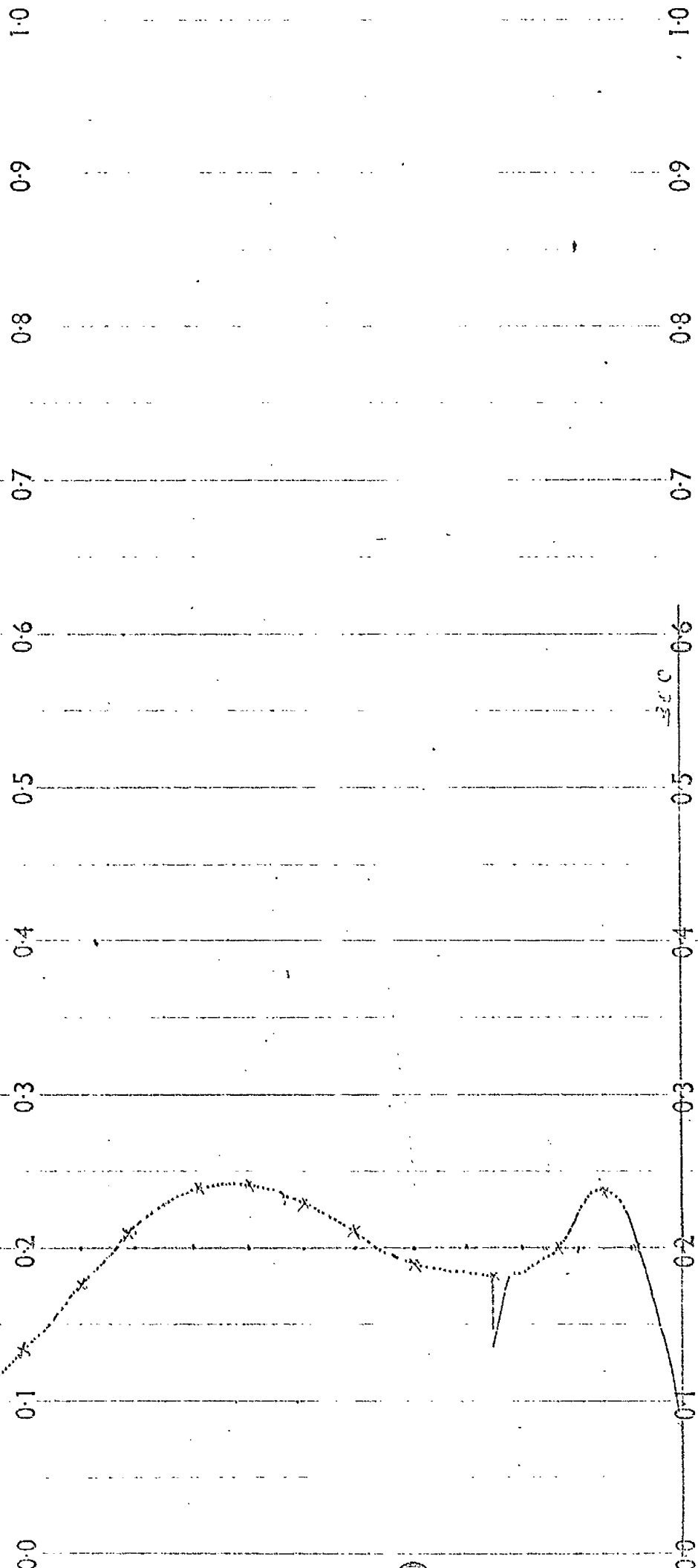


Fig. 77

(Pre-bright yellow 66)

172 After Fixing

SPECTRUM CURVES
on OPTIKA



Fig. 78

Electron micrograph of cellulose film dyed (fixed) with Levafix Brilliant Blue EB, showing the presence of large dye aggregates due to which the film has probably ruptured. (Magnification 30,000)

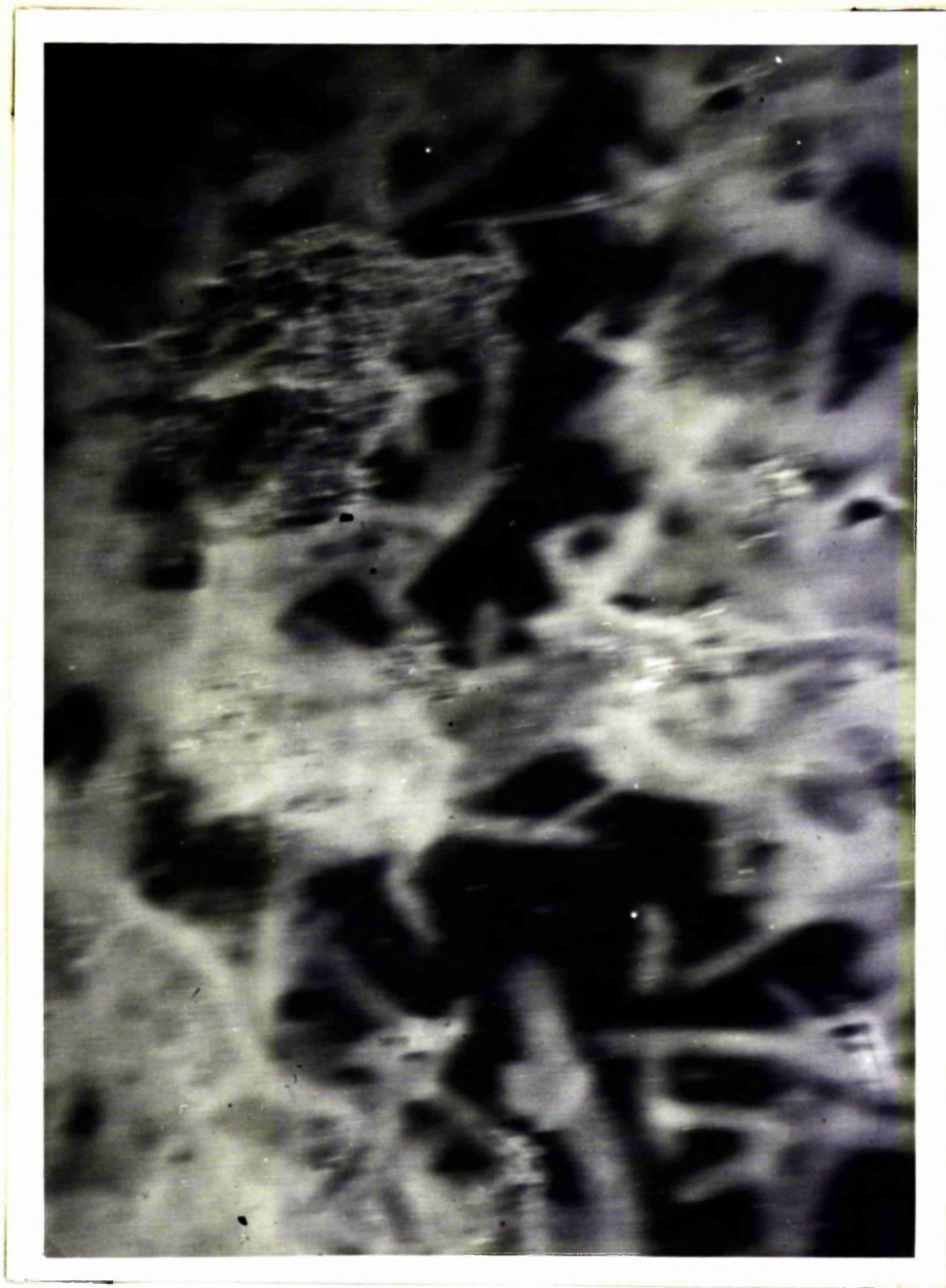


Fig. 79

Electron micrograph of cellulose film dyed (fixed) with Precion Brilliant Orange H-GS, showing the presence of large aggregates due to which the film has probably ruptured. (Magnification 30,000)



Fig. 80

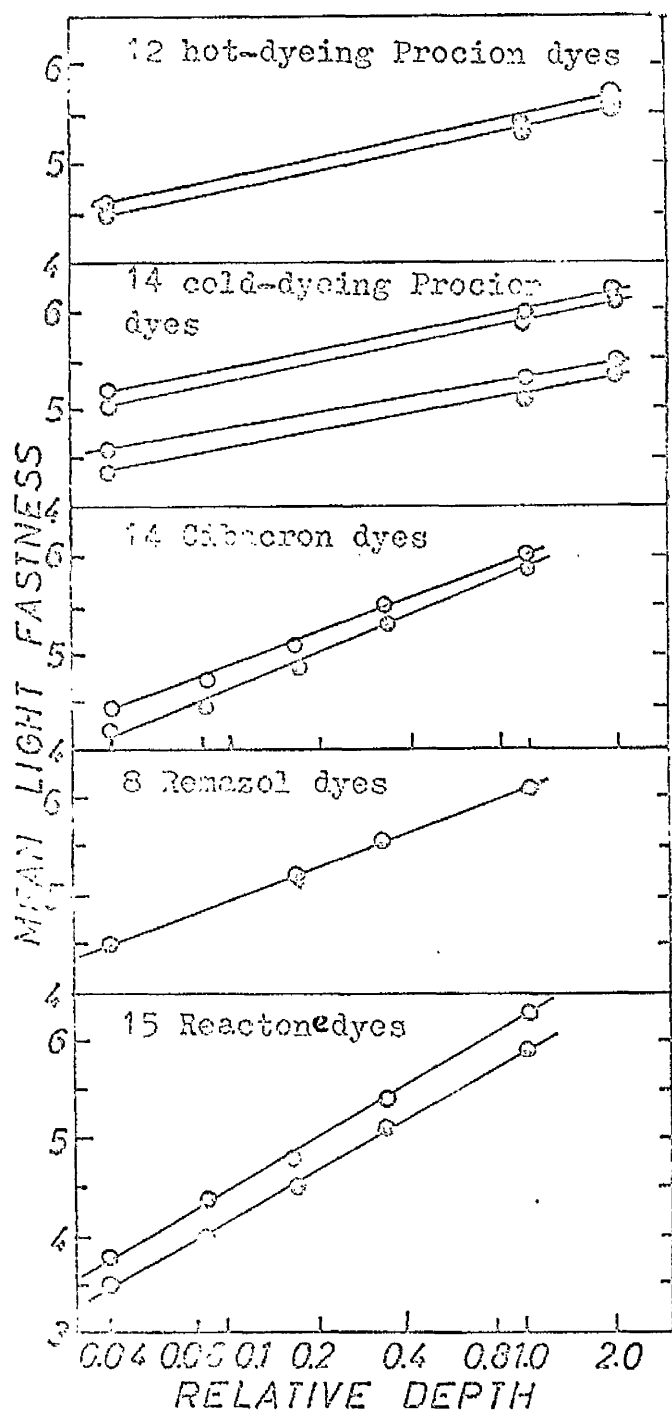
Electron micrograph of cellulose film dyed (fixed) with Procion Brilliant Orange M-GS, showing the presence of large aggregates due to which the film has probably ruptured. (Magnification 30,000)



Fig. 81

Electron micrograph of plain cellulose film.

(Magnification 30,000)



82 Characteristic fastness grade (CFG) curves for dyes on cellulosic substrates.

⊙ Cotton
○ Viscose rayon

(Reproduced with permission from 12)

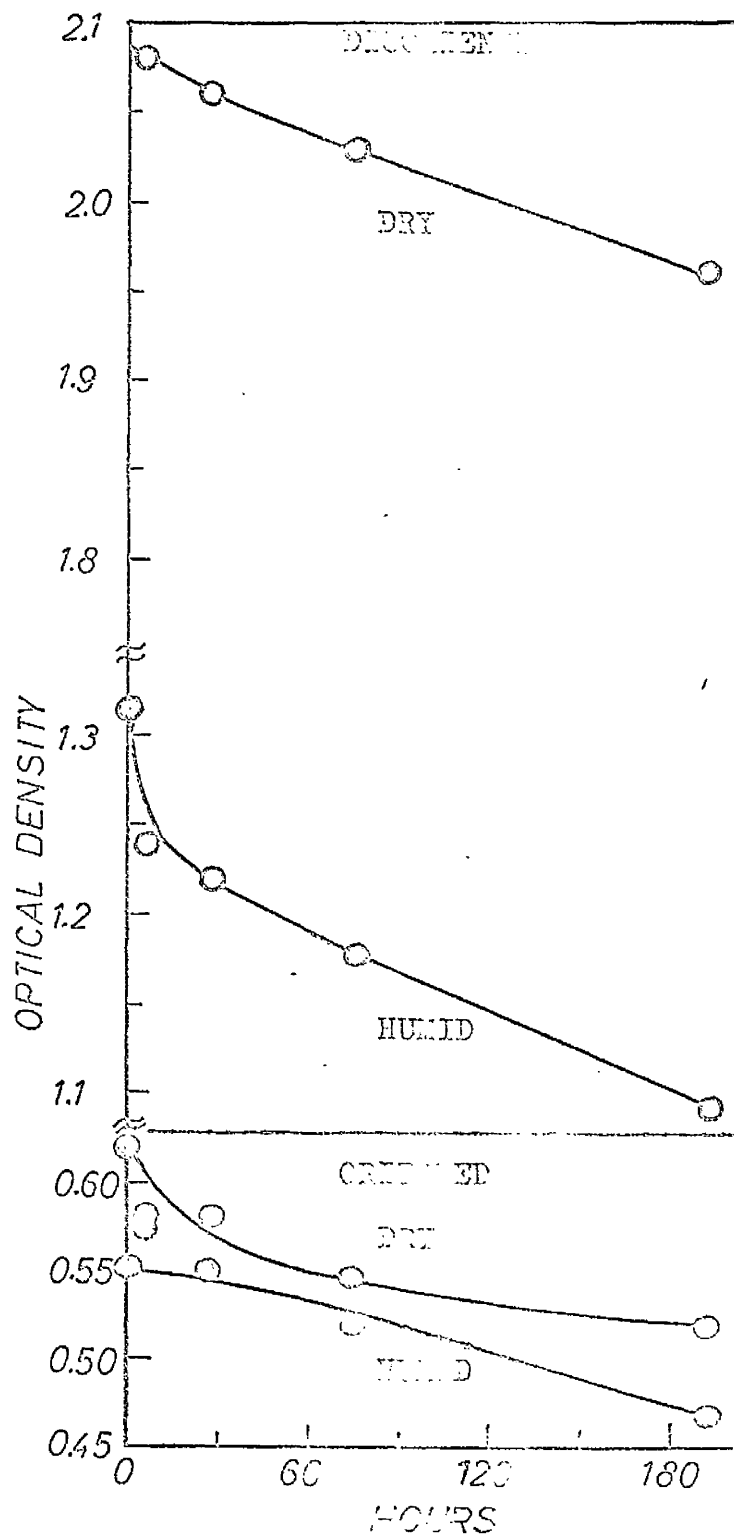


Fig. 83 Fading of Brilliant Violet 10 on dyed dis-orientated film in humid and dry conditions.

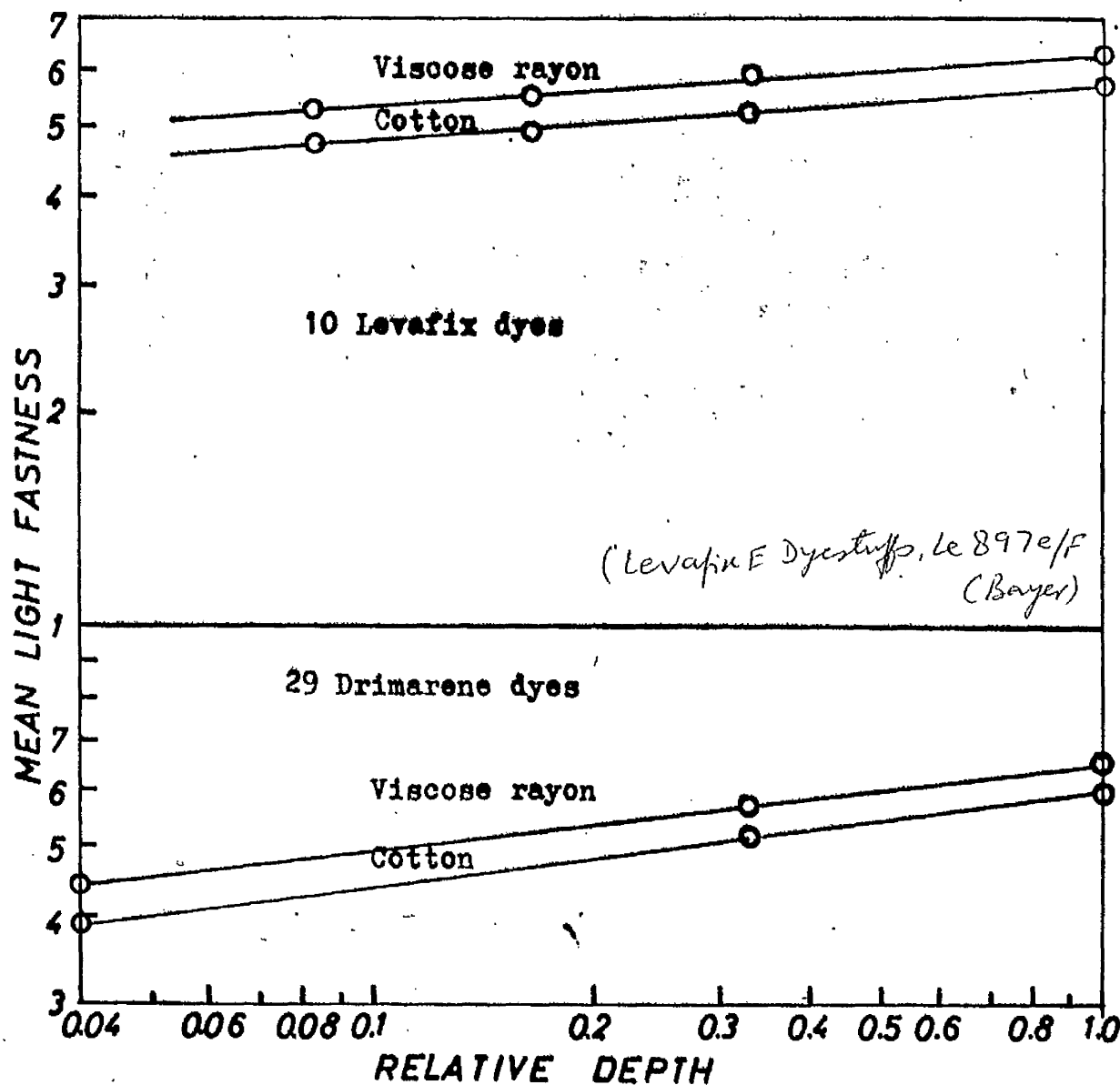


Fig. 84 Characteristic fastness grade (CFG) curves for dyes on cellulosic substrates.

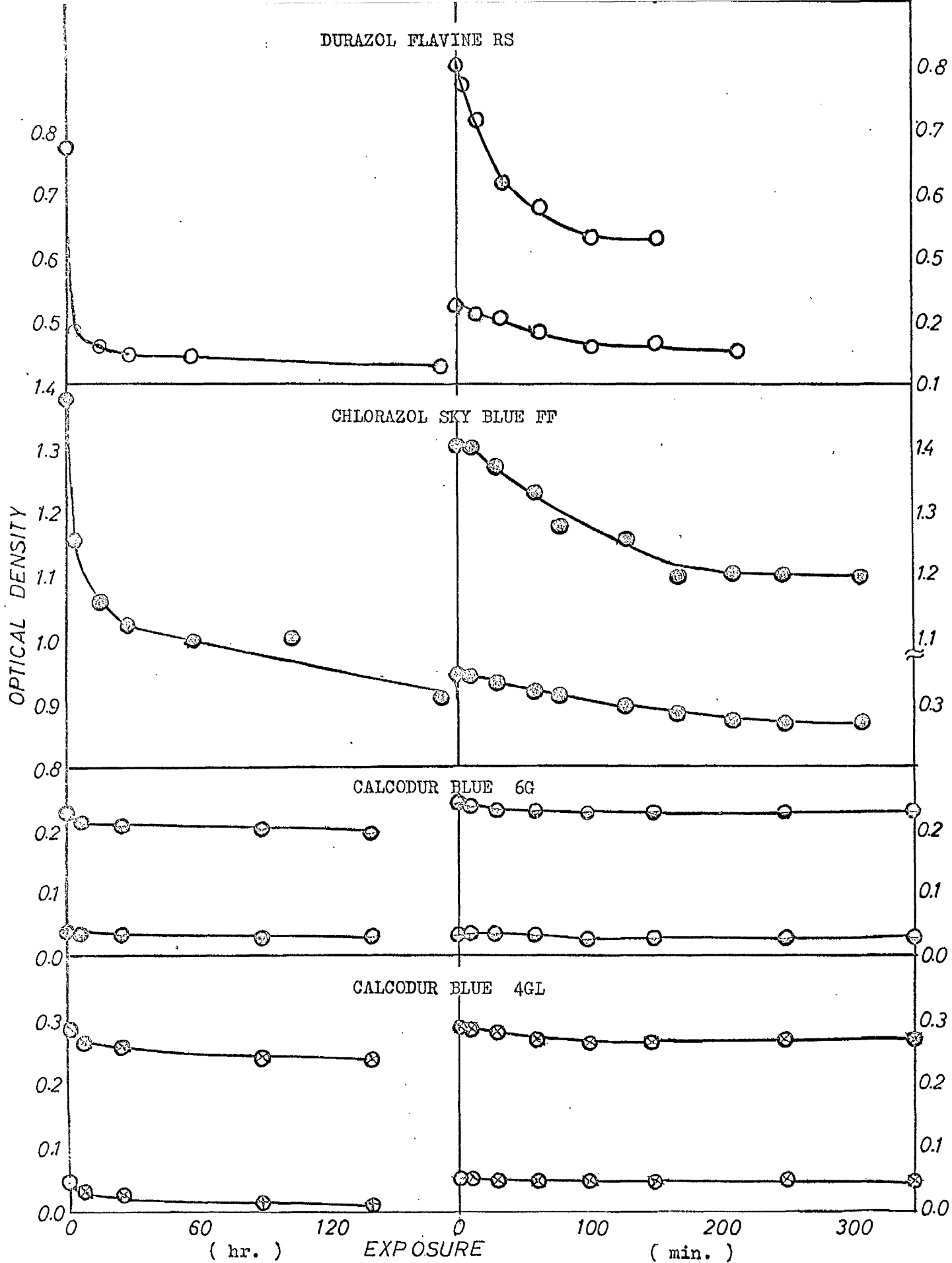


Fig.85 Fading rate curves of direct dyes on Cellophane.

OPTICAL DENSITY

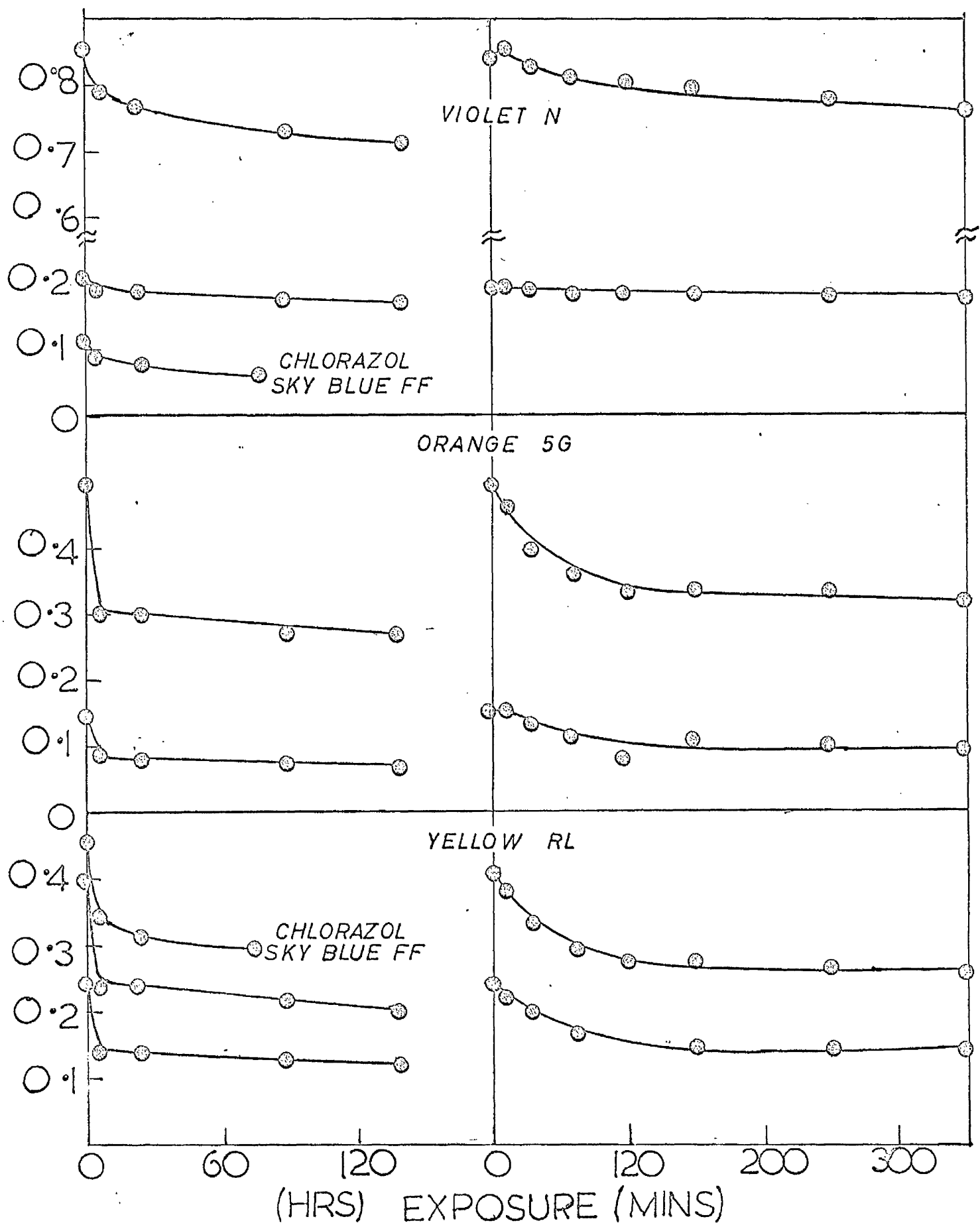


Fig. 86 Fading rate curves of direct dyes (Calcodur) on Cellophane. Two curves of Chlorazol Sky Blue dyes are marked accordingly.

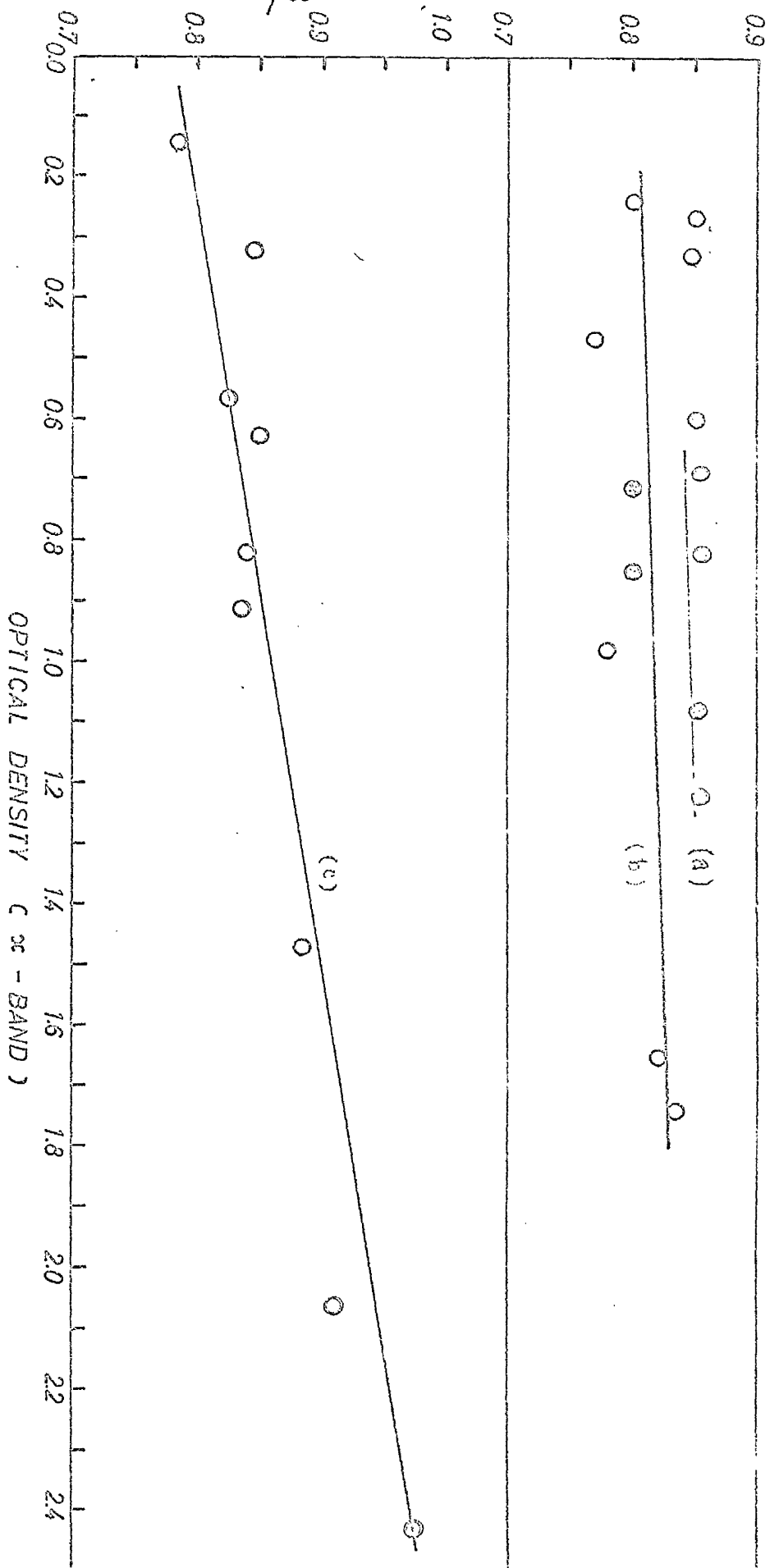


Fig. 84 y/x to x band ratio of Chlorazol Sky Blue FF on (a) gel-Cellophane, and (b) Cellophane, and (c) deionised water.

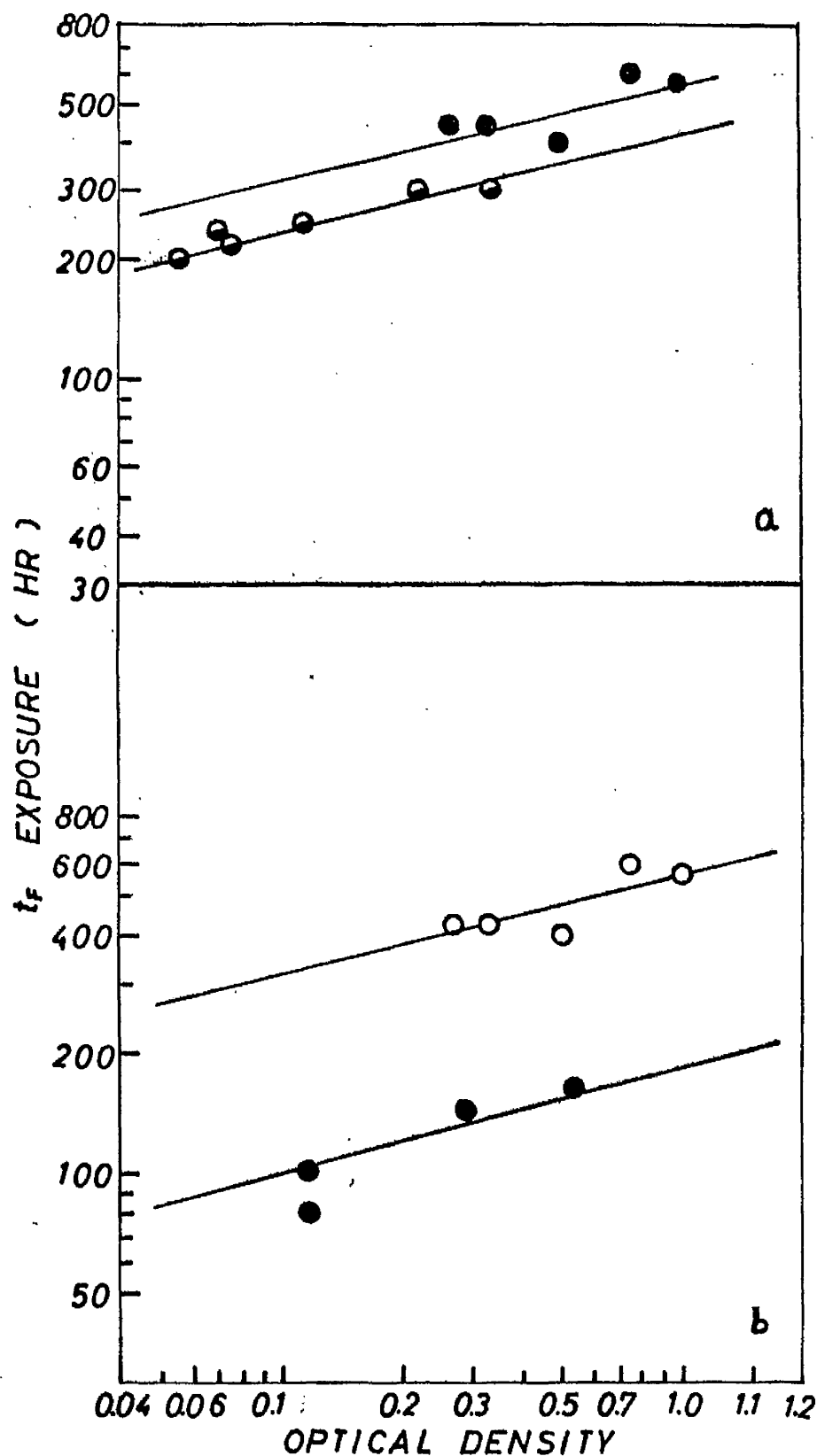


Fig. 87(a) (a) CF curves of Procion Brilliant Yellow 6G on gel Cellophane (●) and Cellophane (◐), both fixed dyeings.

(b) CF curves of Procion Brilliant Yellow 6G on gel Cellophane: ◐ Fixed; ● Unfixed.

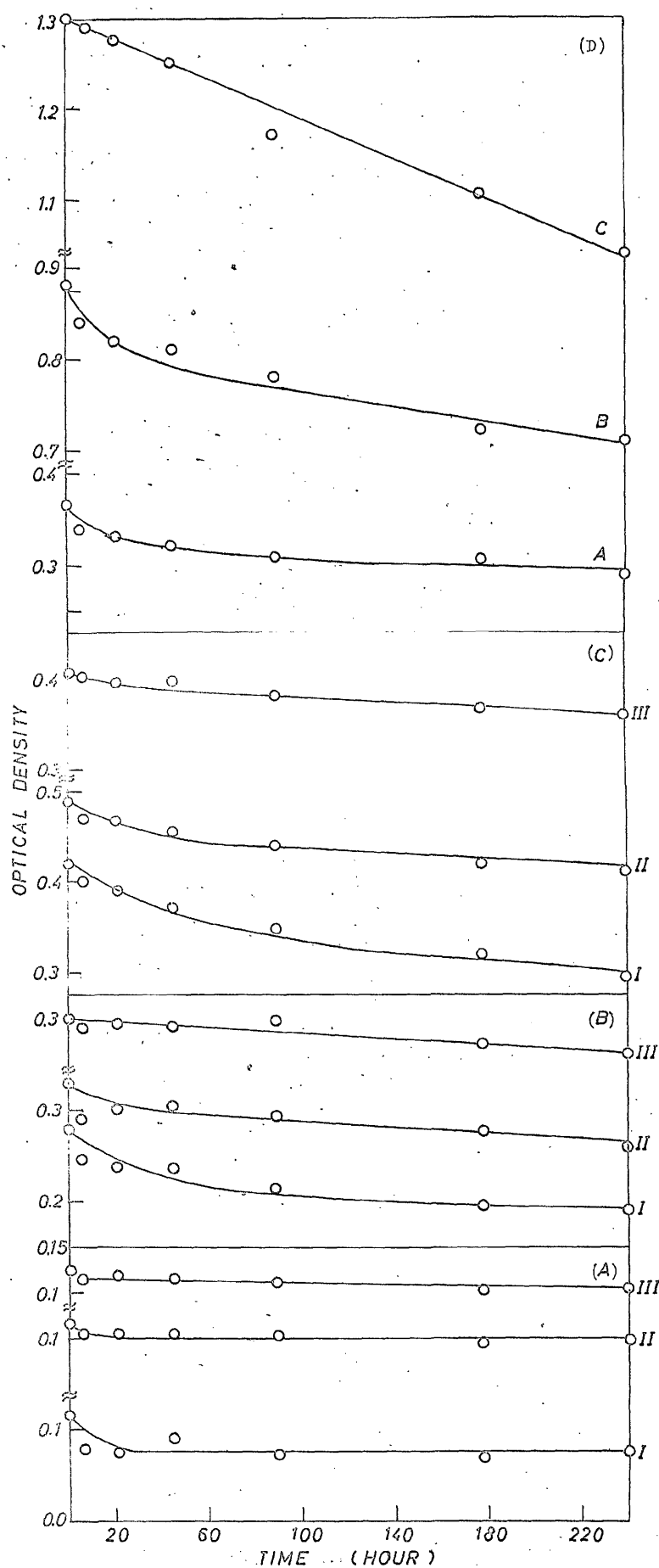
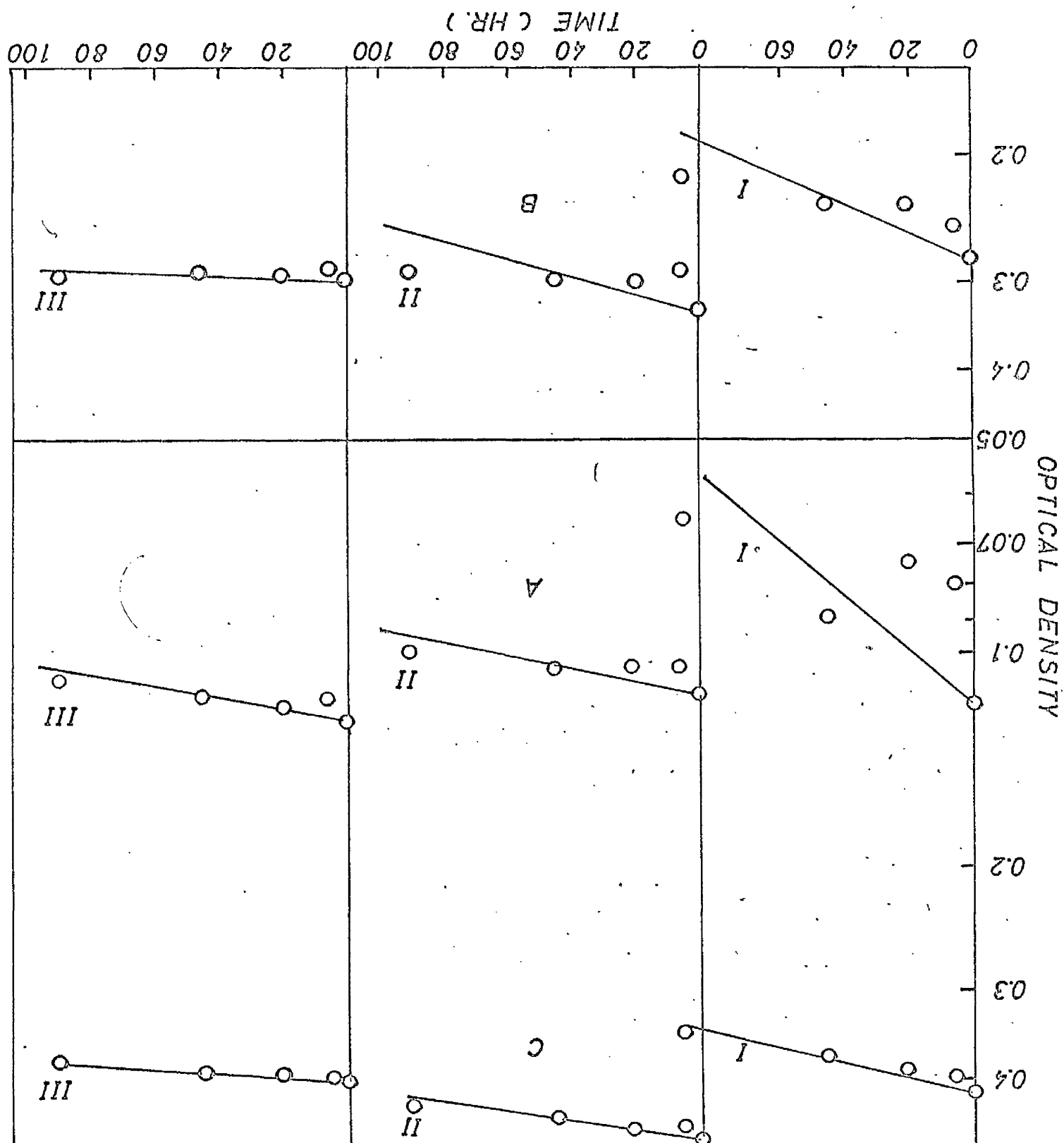


Fig. 88 Fading of Duranol Violet 2R 300 on polyester films in groups of three (I, II & III), I being nearest to lamp, III farthest and II sandwiched in between I and III. Curves I, II & III in boxes (A), (B) and (C) denote fading rates of each film in three groups separately whereas curves A, B and C in box (D) refer to fading rates of the three films I, II and III as one unit.

Fig. 89 Fading of Duranot Violet 2R 500 on polyester films in groups of three (I, II & III), I being nearest to lamp, III farthest and II sandwiched in between I and III:



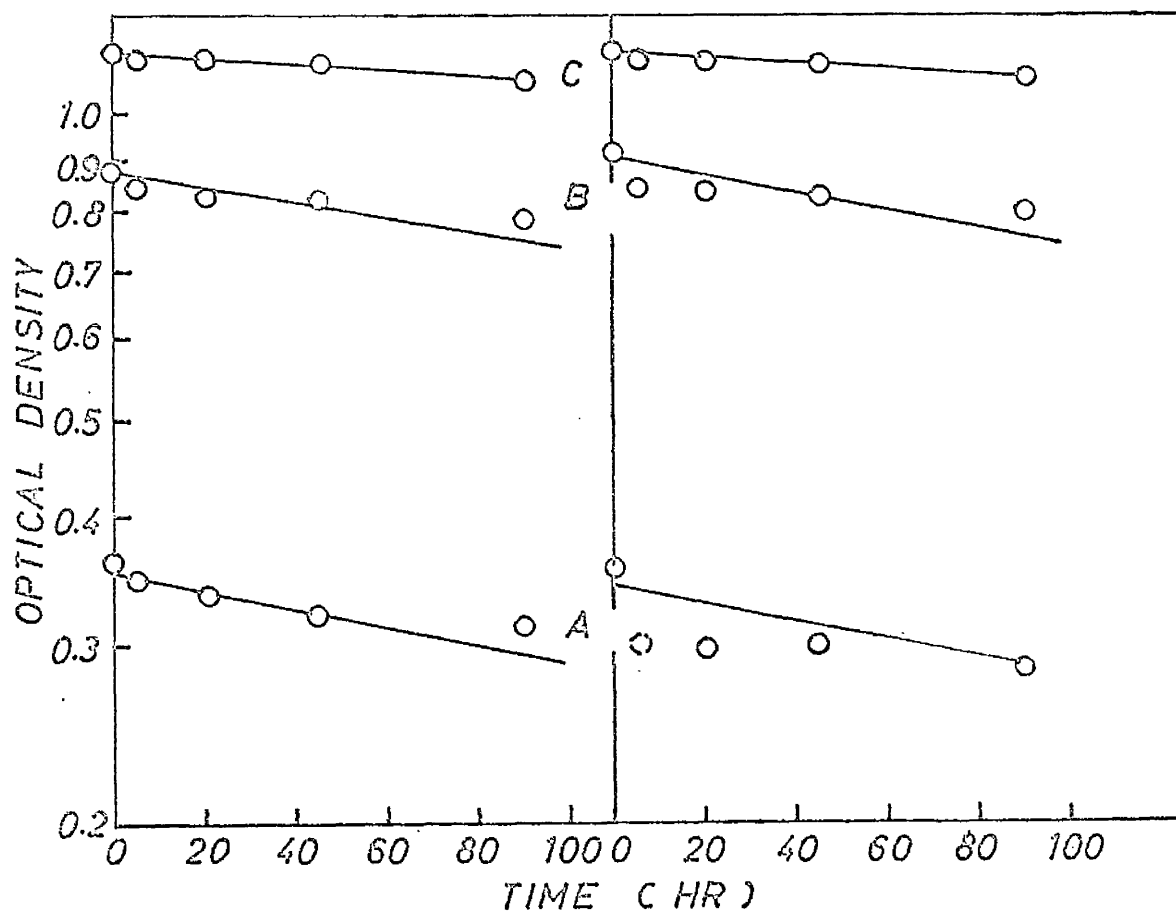


Fig. 90 Curves in the LHS box have been plotted by adding the three O.D. values of the component films of each group; curves on the RHS box refer to fading rates of the three films as one unit.

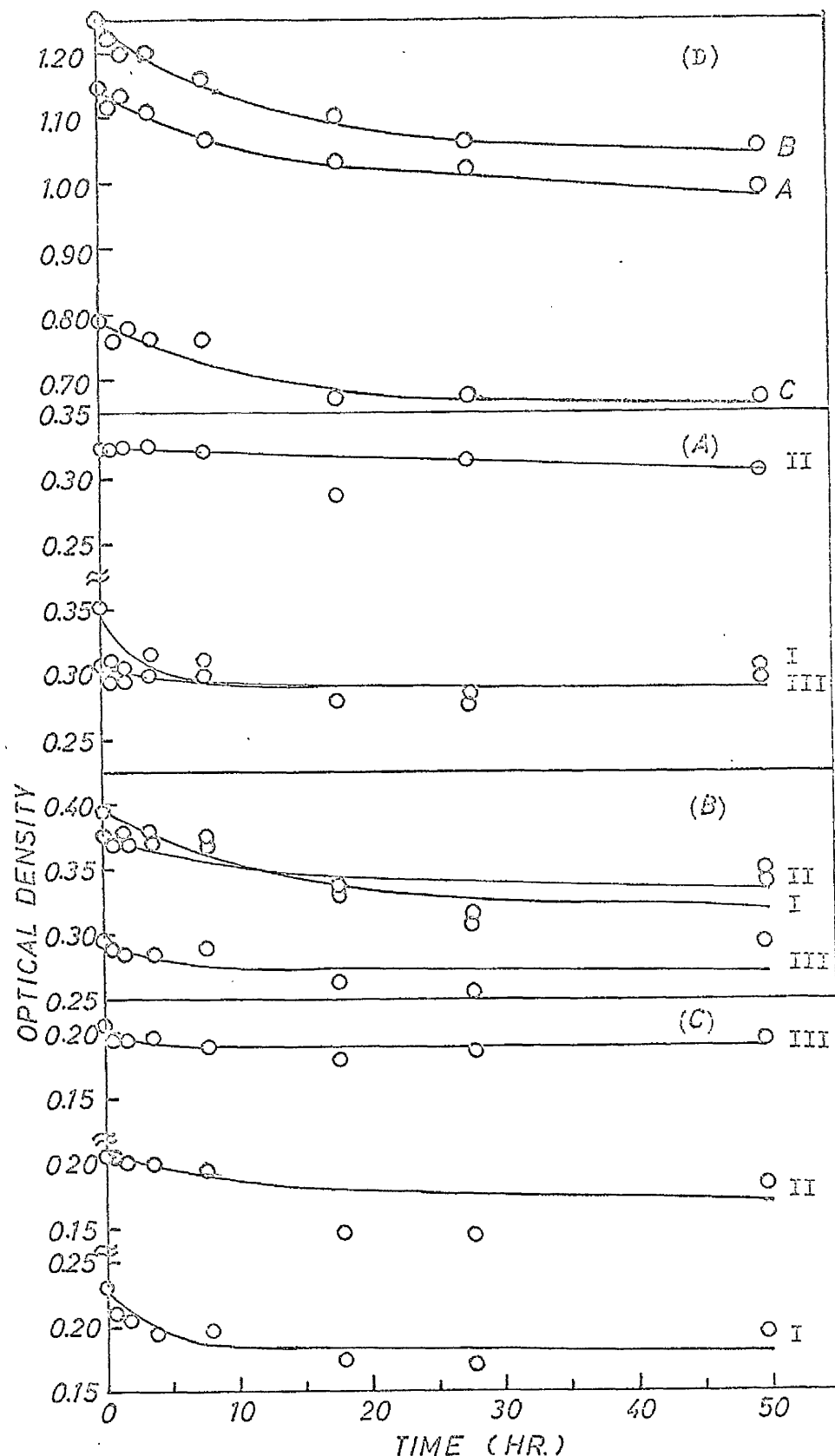


Fig. 91 Fading of Chlorazol Sky Blue FF on Cellophane in groups of three (I, II & III), I being nearest to lamp, III farthest and II sandwiched in between I and III. Curves I, II & III in boxes (A), (B) and (C) denote fading rates of each film in three groups separately whereas curves A, B and C in box (D) refer to fading rates of the three films I, II and III as one unit. Thus $I + II + III$ of (A) gives A of D.

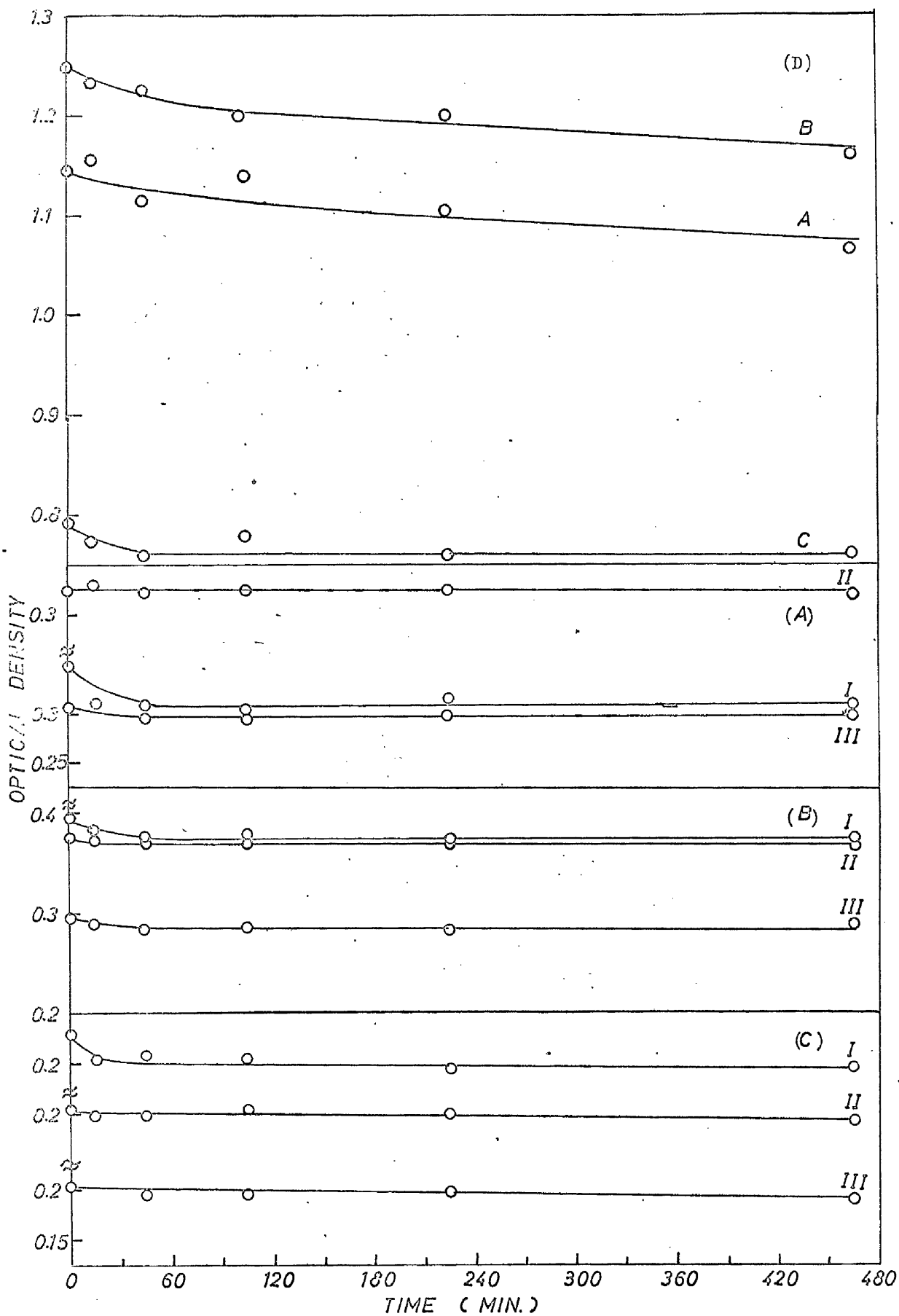


Fig. 92 Fading of Chlorazol Sky Blue FF on Cellophane. Details same as in Figure 91, except that time is in minutes.

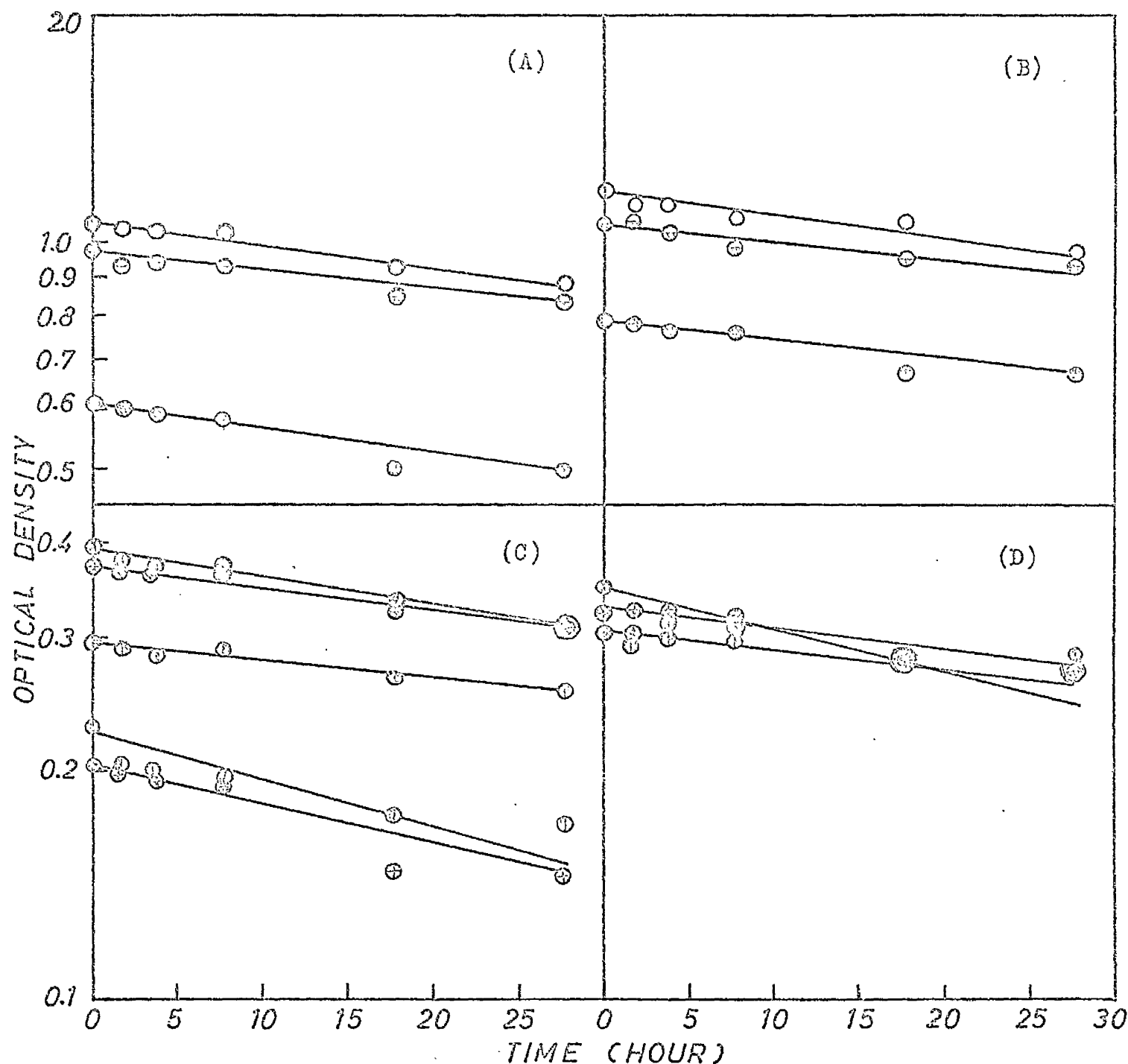


Fig. 93 Fading of Chlorazol Sky Blue FF on Cellophane in groups of three (I, II and III), I being nearest to lamp, III farthest and II sandwiched in between the I and III. Curves in boxes (C) & (D) denote fading rates of each film in three groups separately; curves in box (B) refer to fading rates of the three films as one unit; curves in box (A) have been plotted by adding the three Optical Density values of the component films of each group.

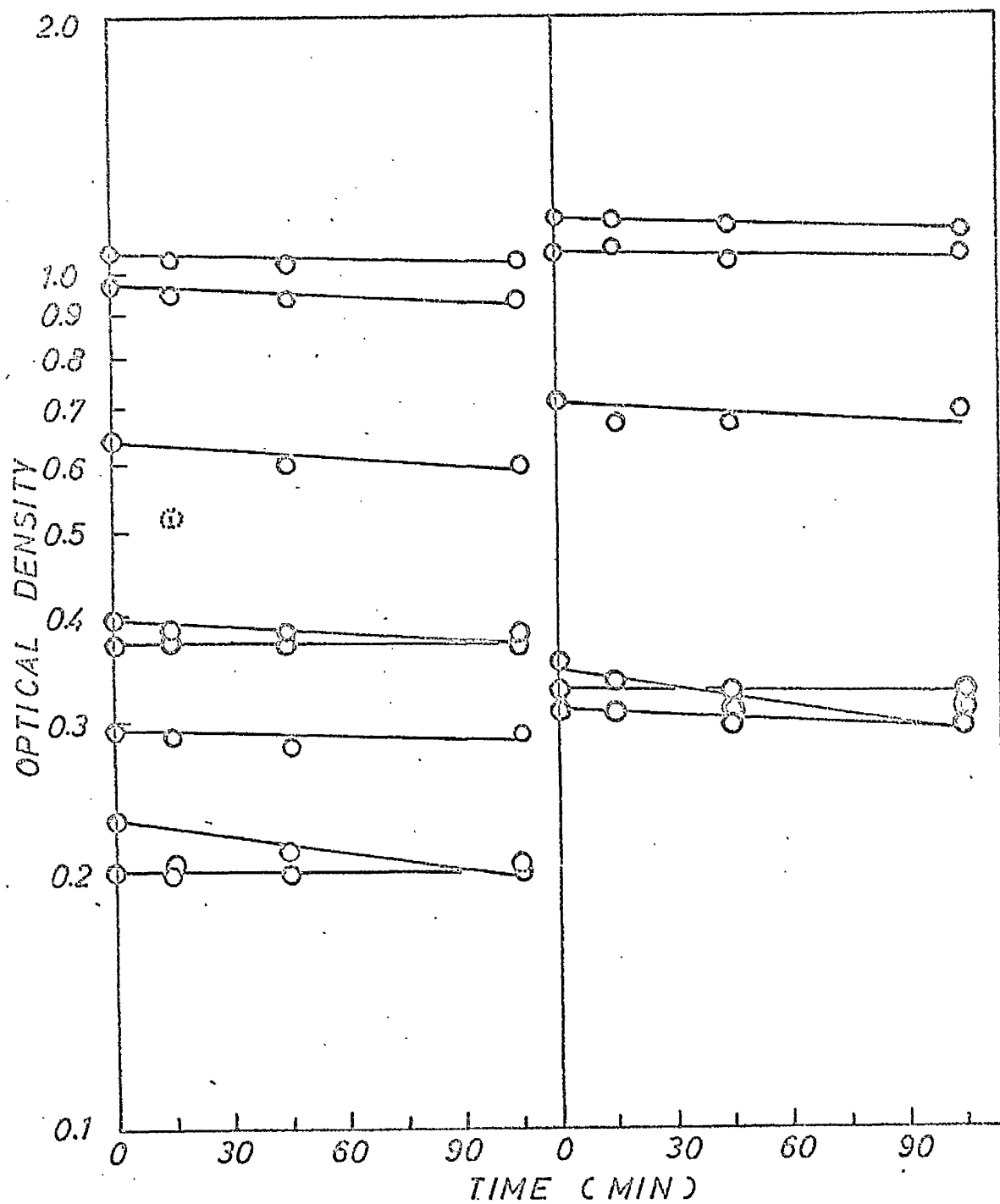


Fig.93(a) Details same as for Figure 93.

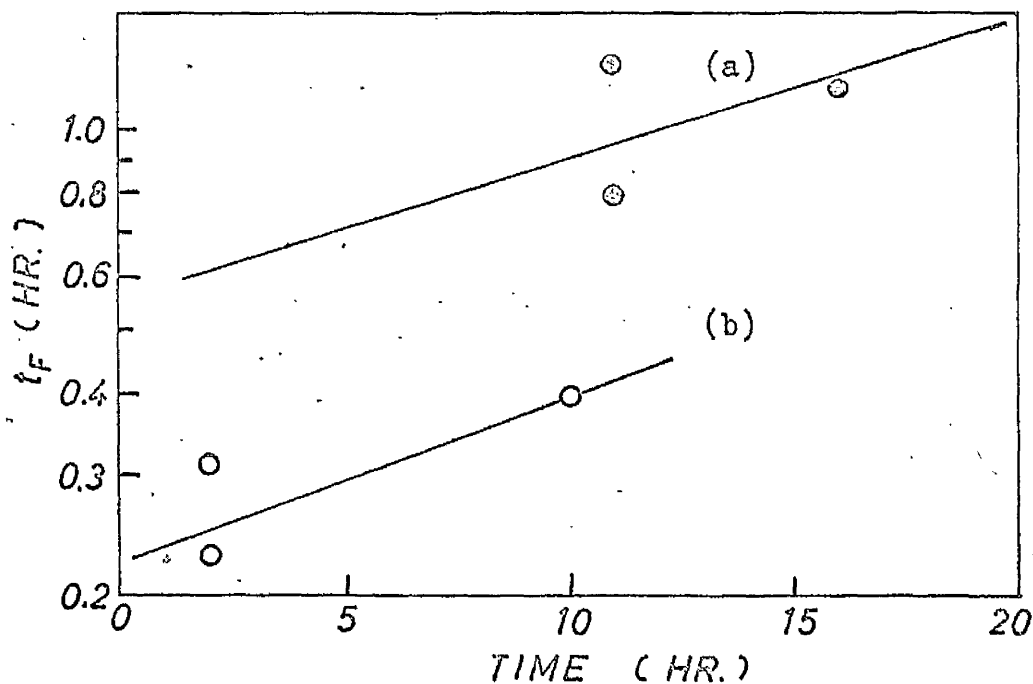


Fig. 94 CF curves of Chlorazol Sky Blue FF on Cellophane.

(a) corresponds to curves A, B, and C in box (D) of Fig. 91 whereas (b) refers to curves (A I), (B I) & (C I).

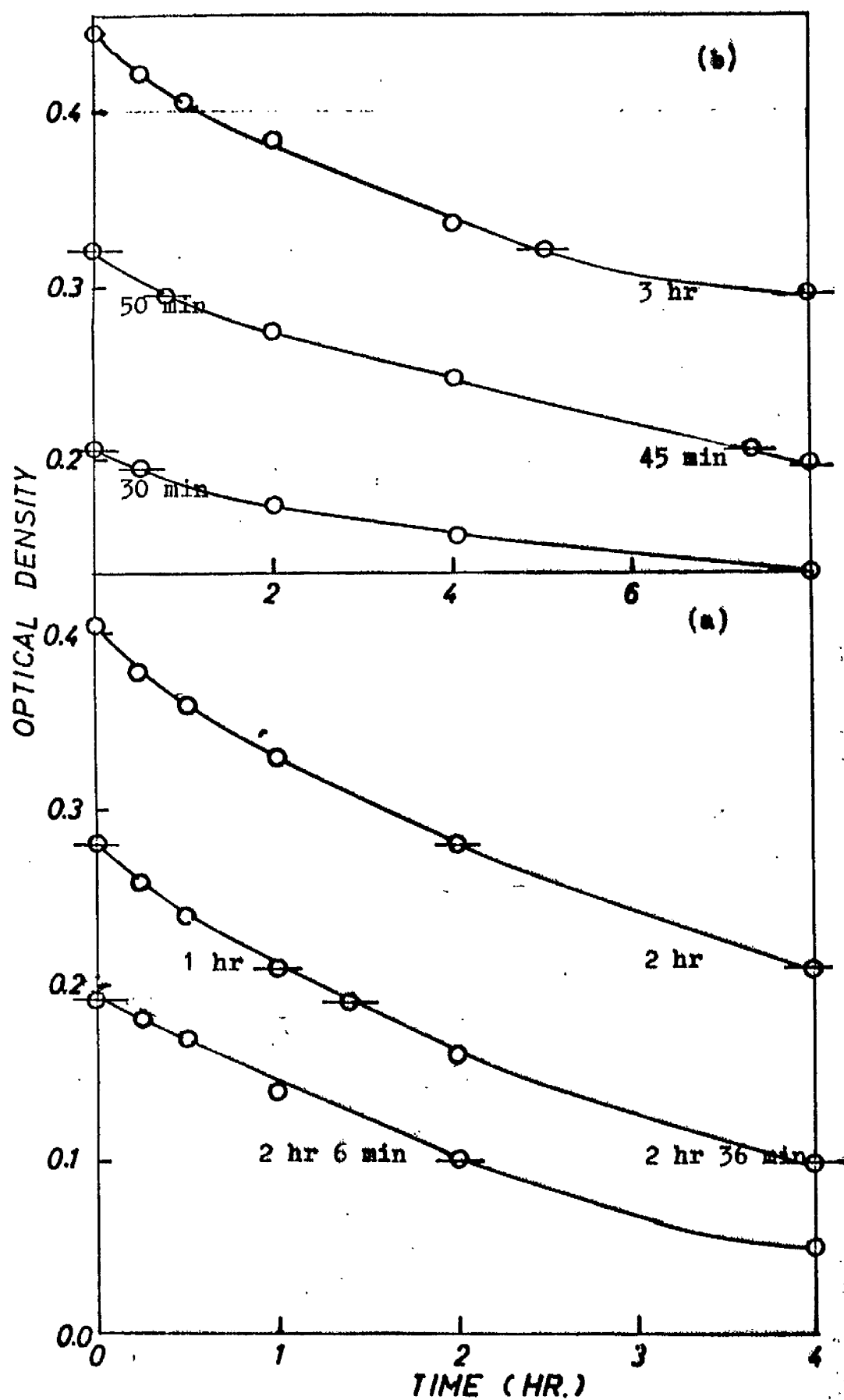


Fig. 95 Fading rate curves for 2:4-dichloroaniline — R Acid on (a) Cellulose, and (b) Gel.

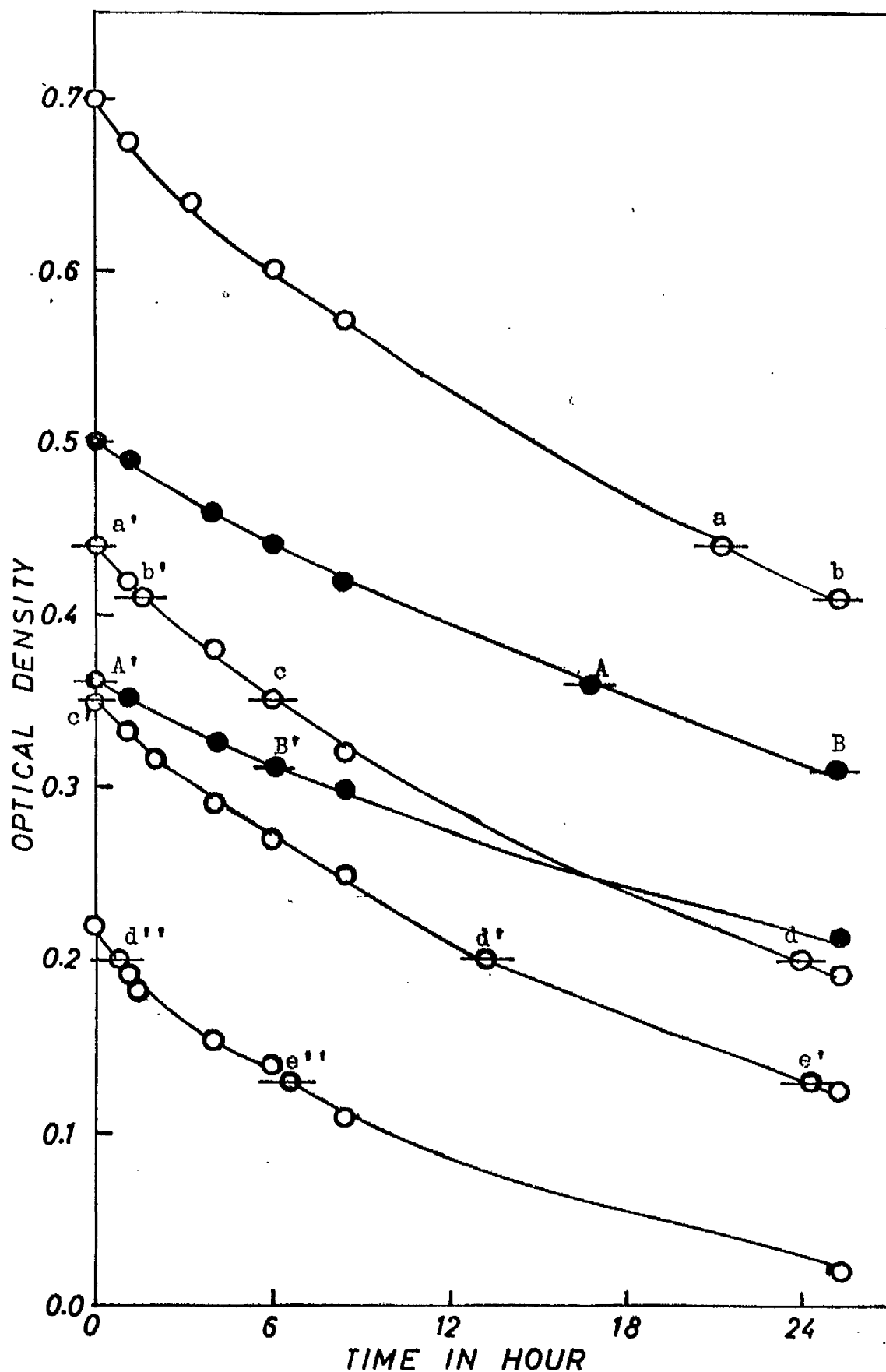


Fig. 96 Fading rate curves for p-chloro-aniline —
R Acid on ○ gel and ● Cellofas.

Time of fading from: a - b 3 hr 54 min;
a' - b' 2 hr 24 min; c - d 17 hr 20 min;
c' - d' 13 hr 12 min; d' - e' 11 hr 6 min;
d'' - e'' 6 hr; A - B 8 hr 24 min; A' - B'
6 hr 18 min.

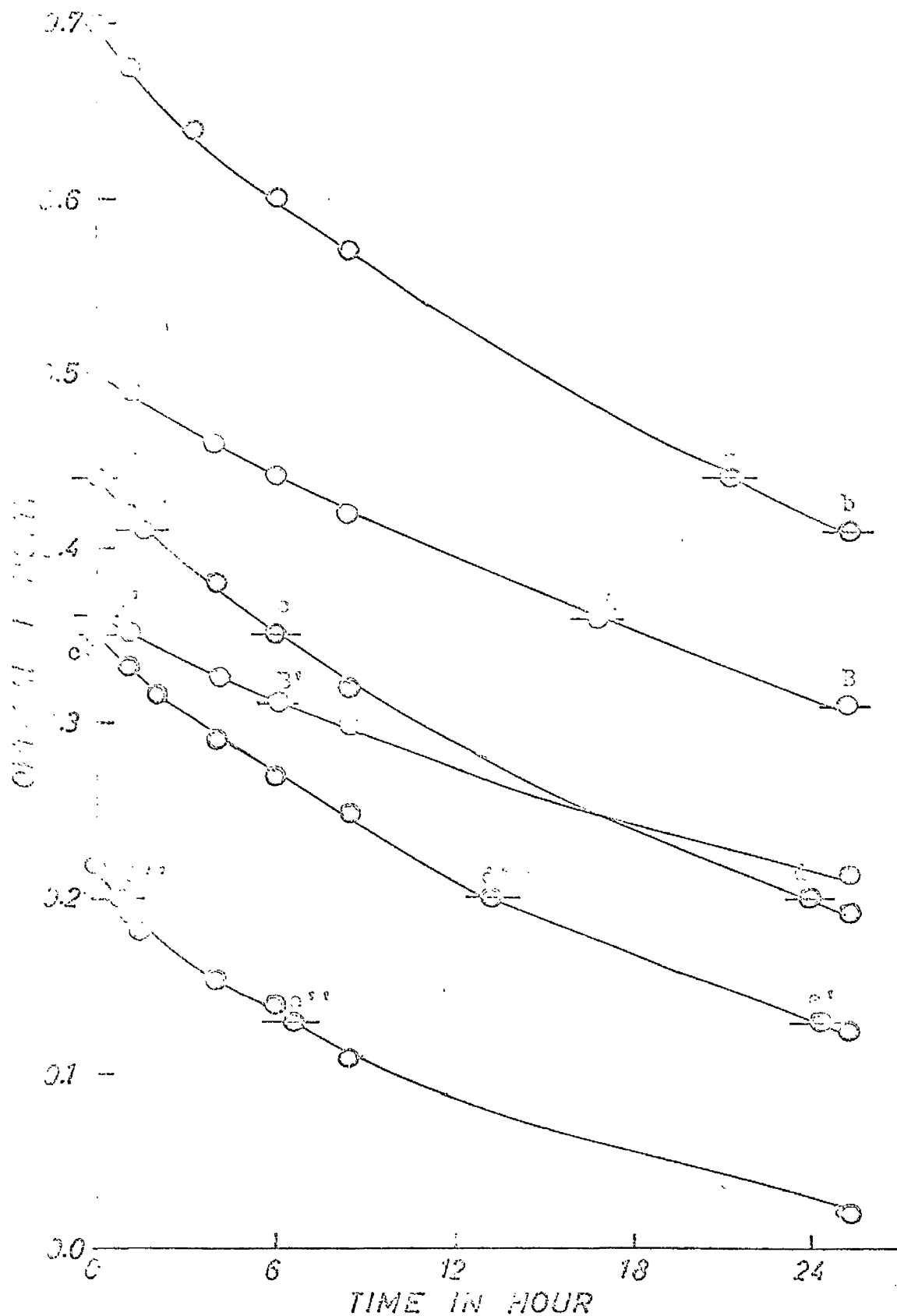


Fig. 97 Fading rate curves for p-chloro-aniline ---
H Acid on \bigcirc gel and \bigcirc Cellofas.

Time of fading from: a - b 3 hr 54 min;
a' - b' 2 hr 24 min; c - d 17 hr 20 min;
c' - d' 13 hr 12 min; d' - e' 11 hr 6 min;
d'' - e'' 6 hr; A - B 3 hr 24 min; A' - B'
6 hr 18 min.

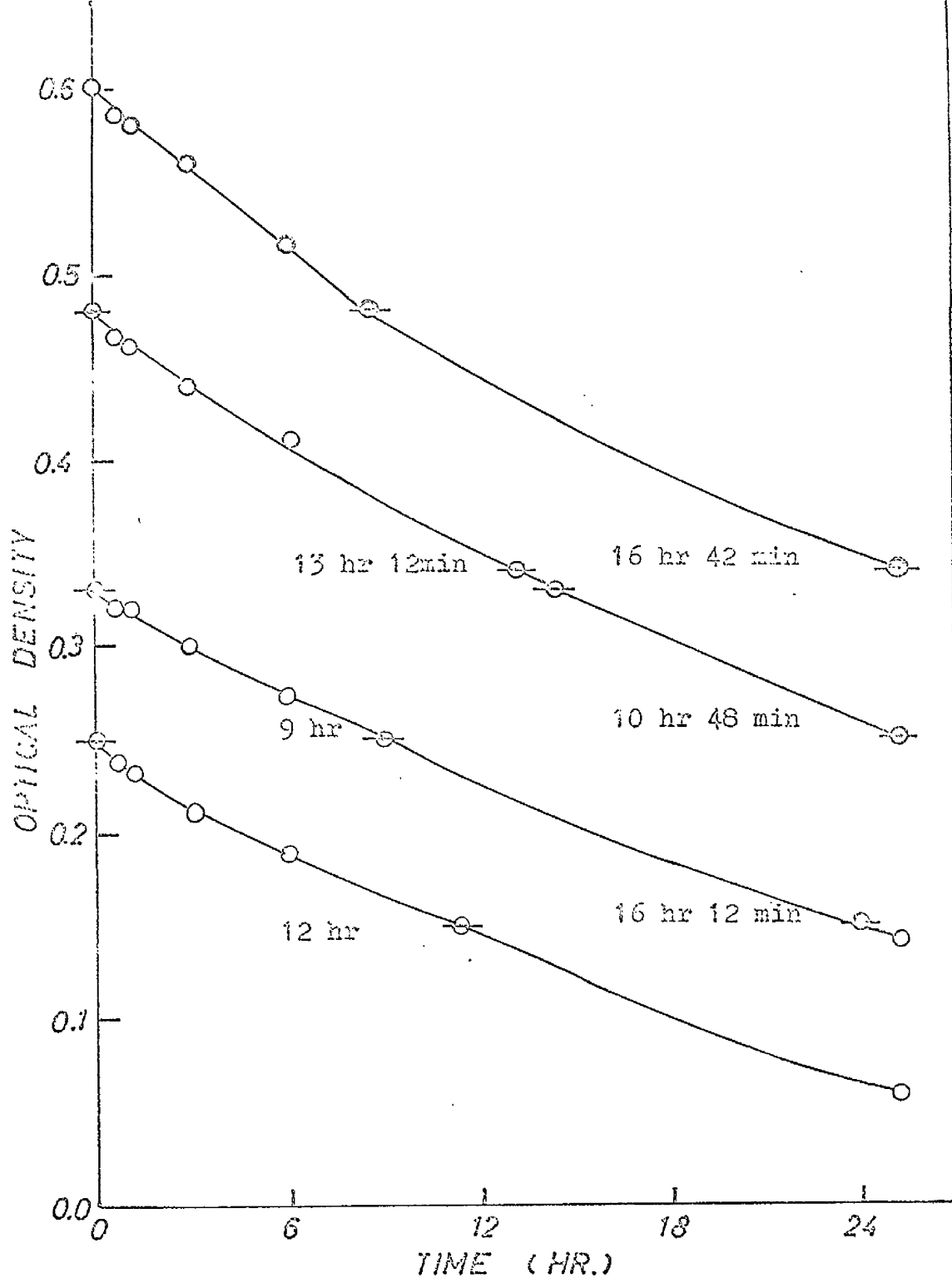


Fig. 98 Fading rate curve for Aniline — R Acid on Cellofas.

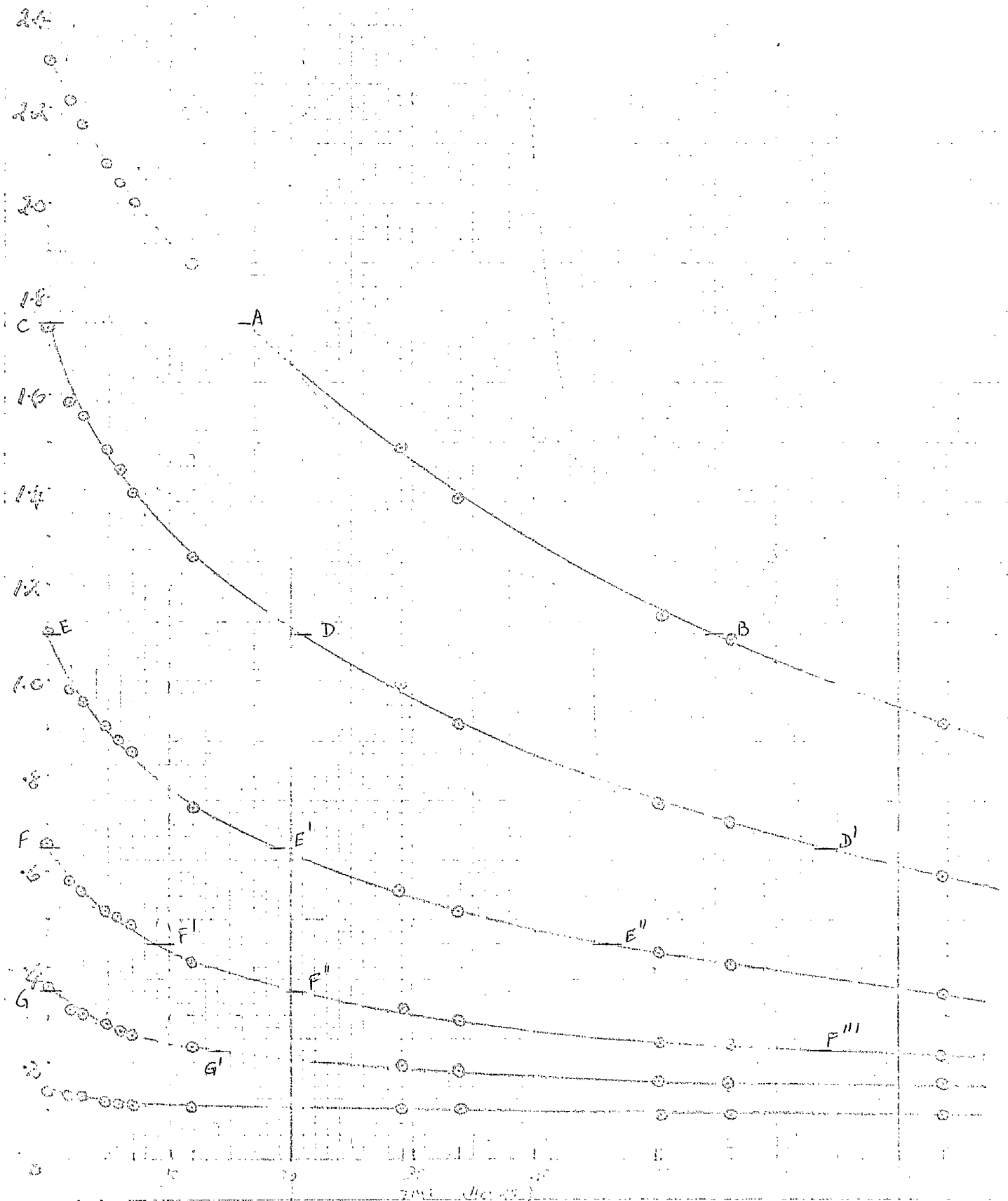


Fig. 99

From	
$A \rightarrow B$	39 hrs.
$C \rightarrow D$	21 hrs.
$D \rightarrow D'$	43 hrs.
$E \rightarrow E'$	19 hrs.
$E' \rightarrow E''$	27 hrs.
$F \rightarrow F'$	9 hrs.
$F'' \rightarrow F'''$	42 hrs.
$G \rightarrow G'$	14 hrs.

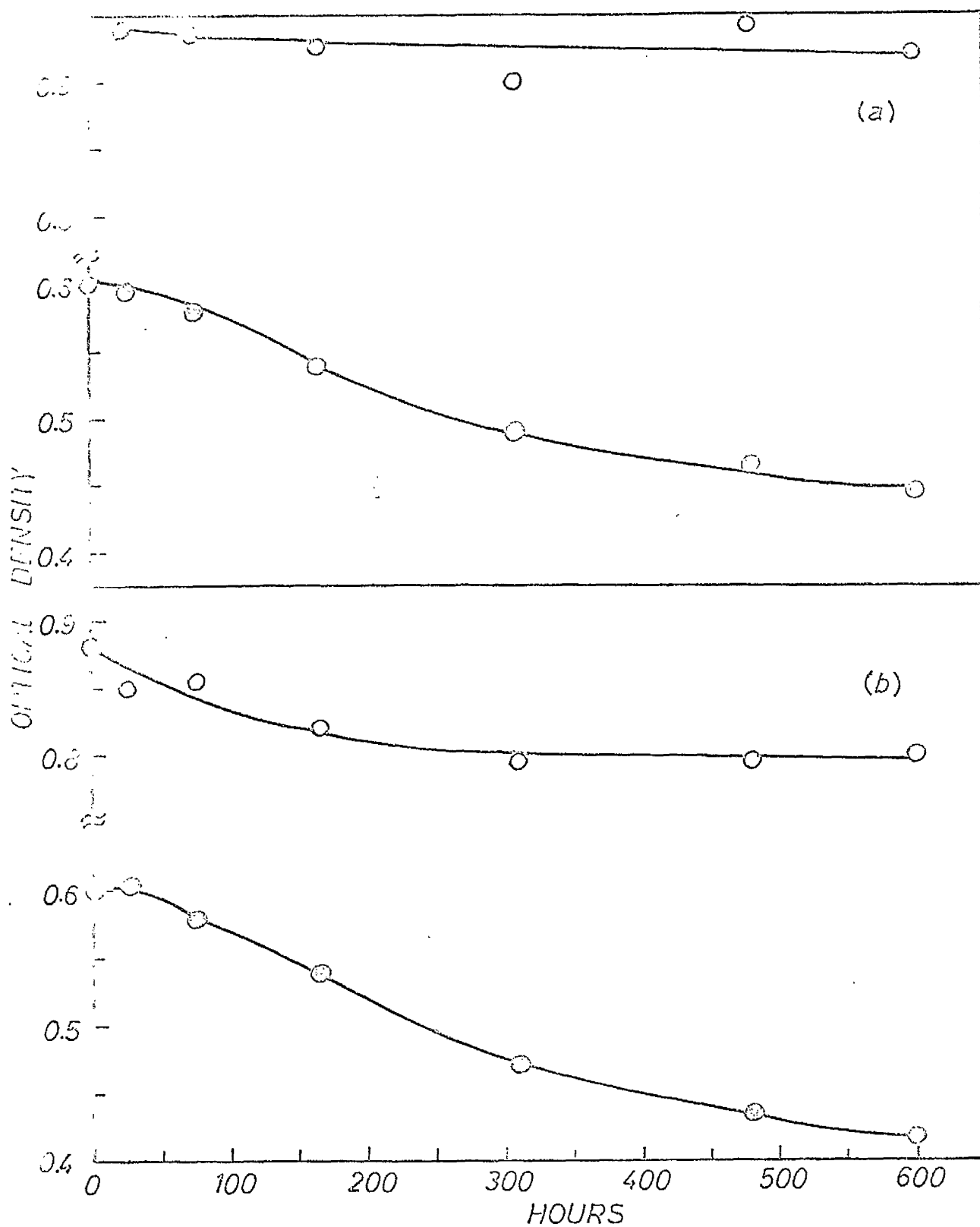


Fig.100 Fading of oriented and disoriented polyester films under (a) dry, and (b) humid conditions.

○ Oriented.

○ Disoriented.

Dye = Serisol Brilliant Violet 2R

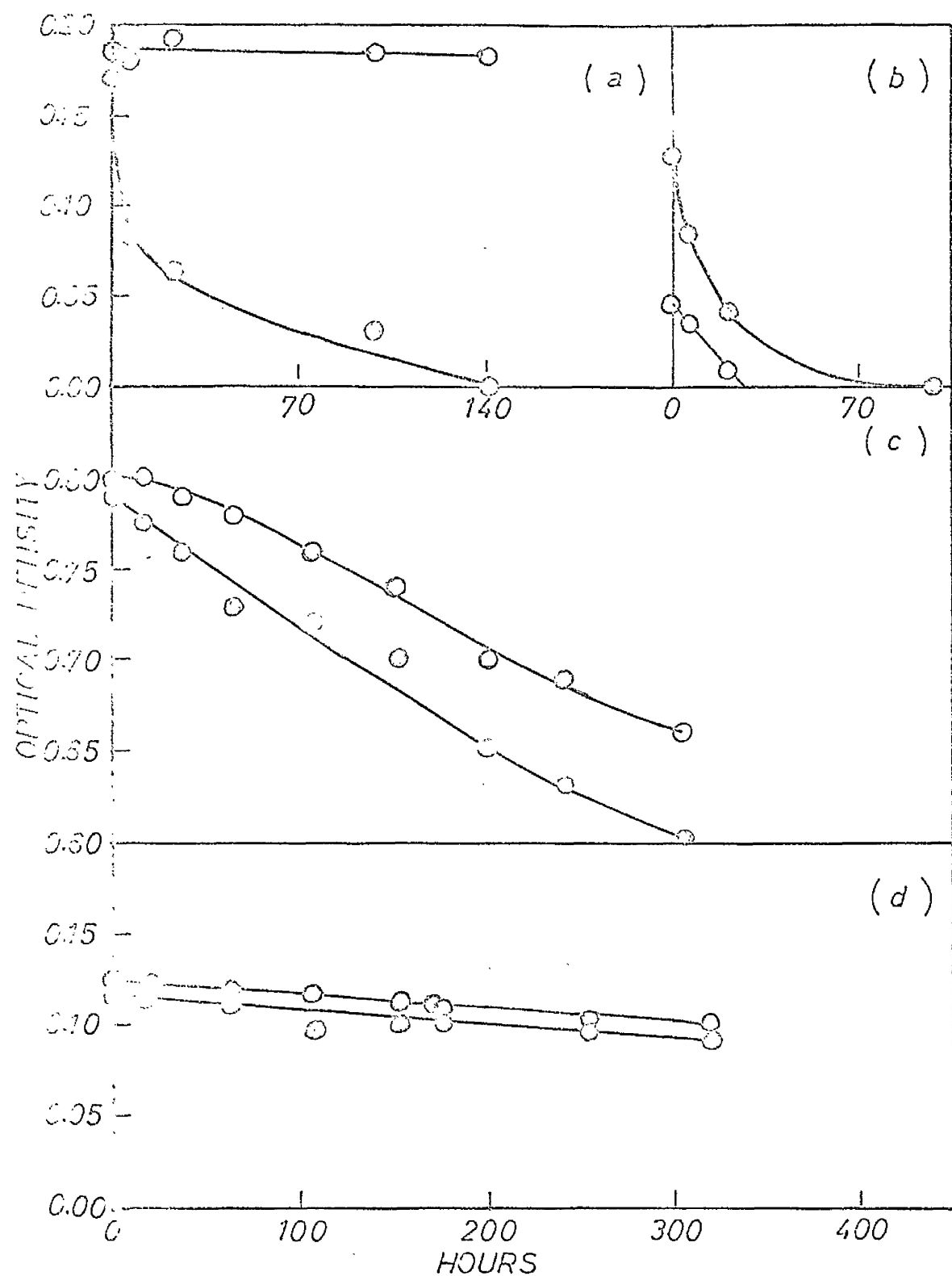


Fig. 101 Fading of Serisol Brilliant Violet 2R on polyester film. (a) & (b) disoriented; (c) oriented; (d) disoriented by boiling in water for three hours.
 O Fading under dry conditions.

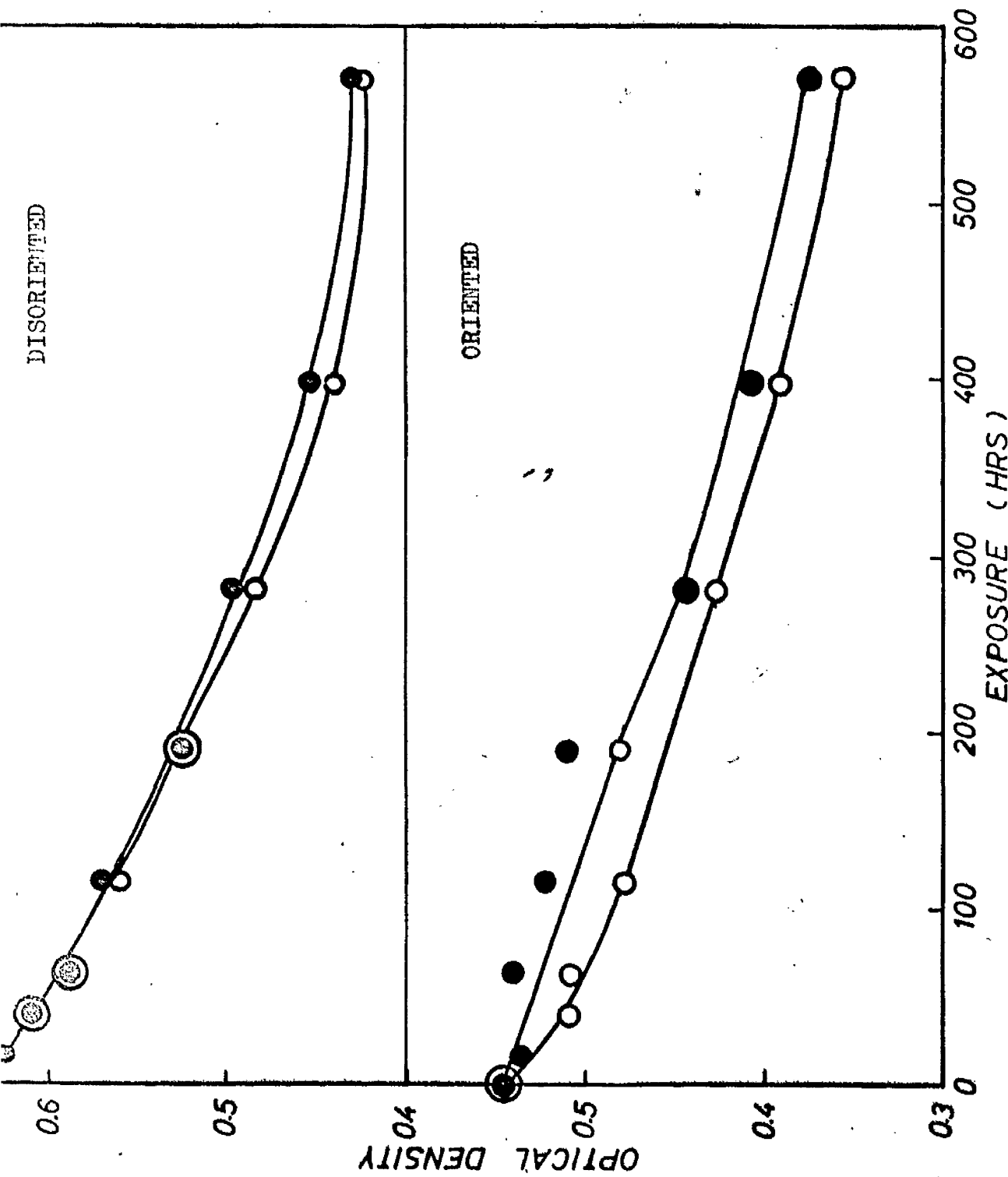


Fig. 102 Fading of Serisol Brilliant Violet 2R in oriented and disoriented polyester film in dry and humid conditions.

● Dry; ○ Humid.

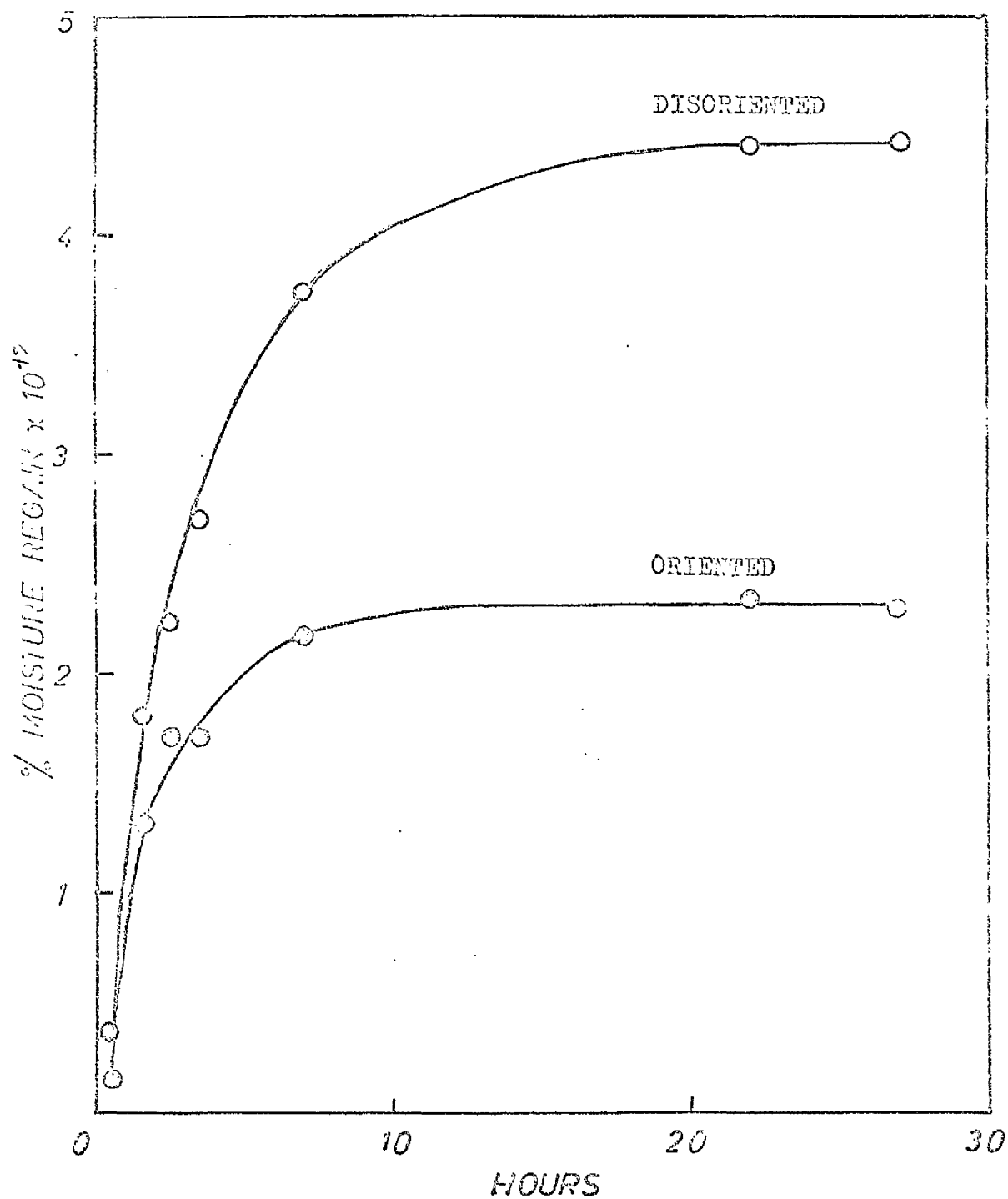
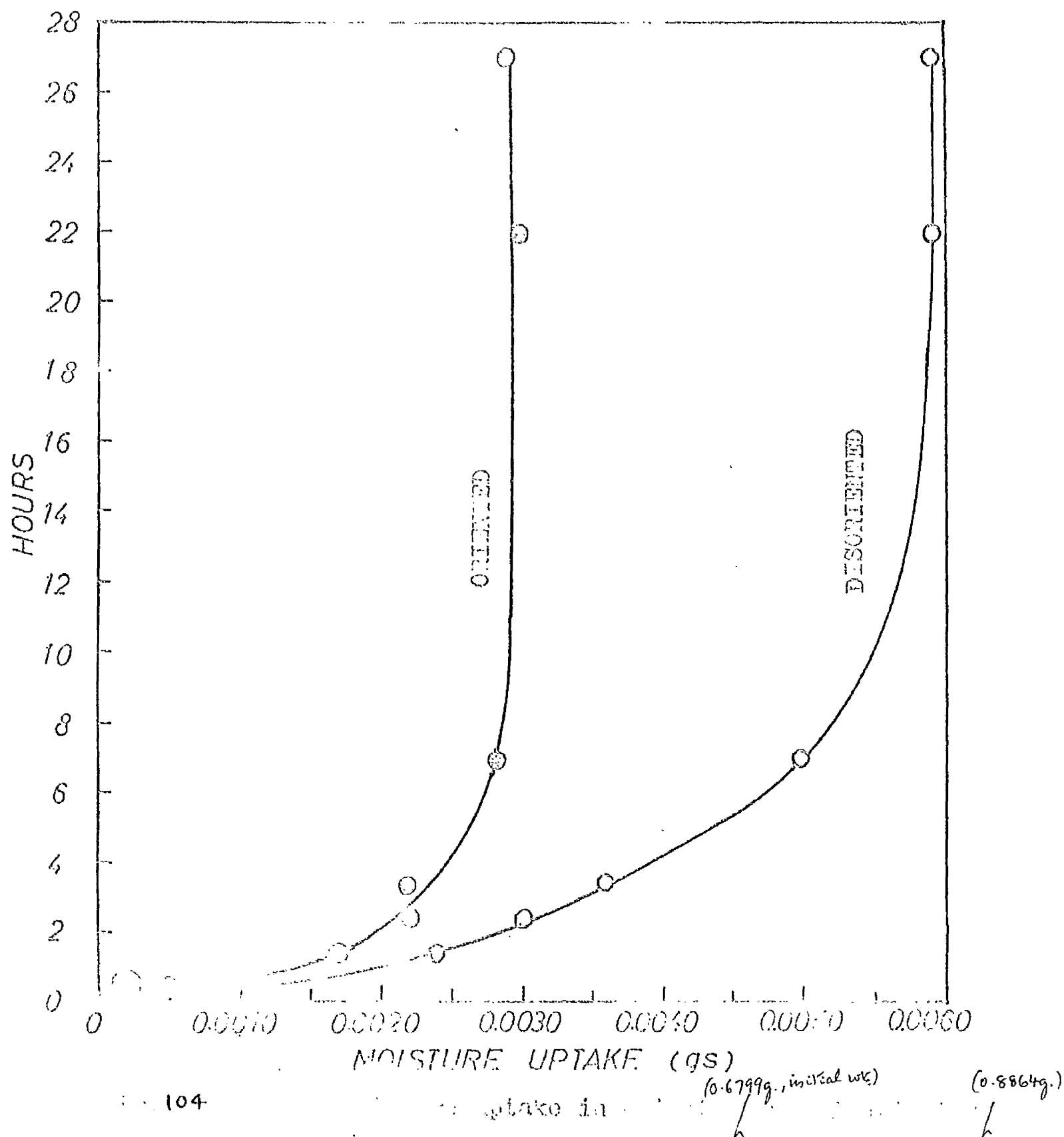


Fig. 103 Percentage moisture regain on oriented and disoriented polyester film.



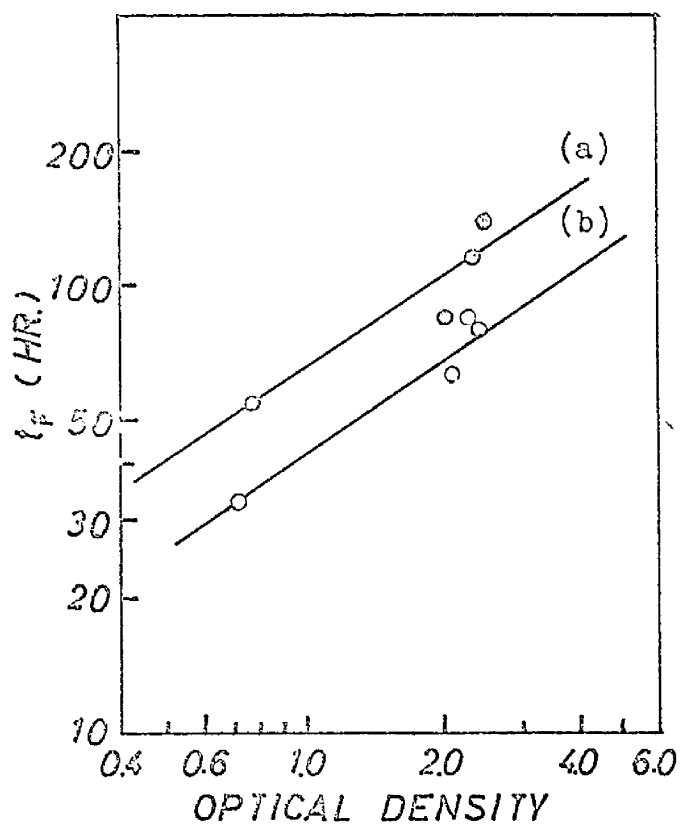


Fig.105 CF curves of Dispersol Fast Orange A150 Pdr. on Cellulose Triacetate sandwiched between (a) Polyester, and (b) Cellulose Triacetate.

105



Fig. 106

Electron micrograph of plain cellulose
triacetate film. (Magnification 30,000)

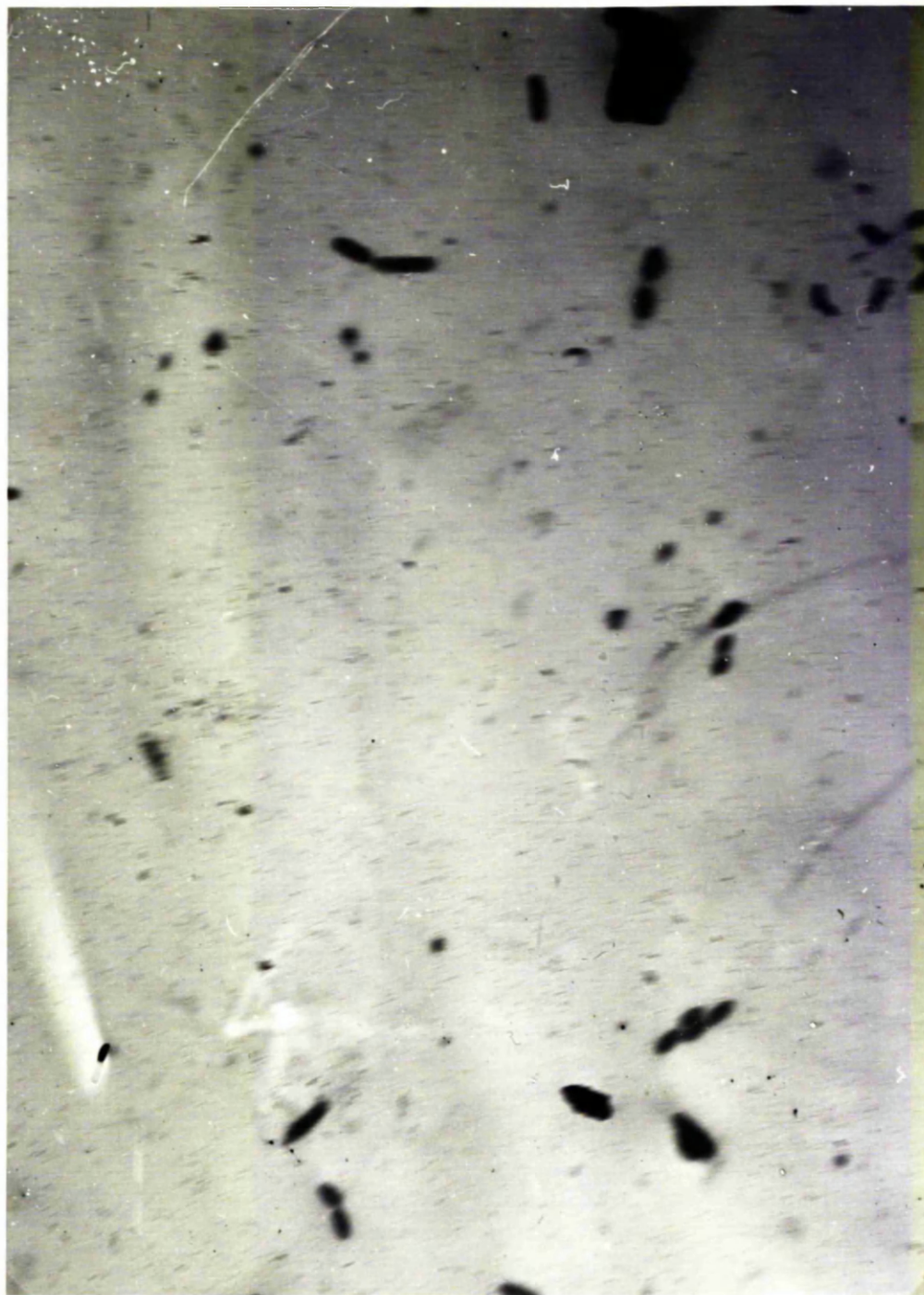


Fig. 107

Electron micrograph of cellulose triacetate film
dyed with Duranol Violet 2R 300 Powder Fine,
showing the presence of dye aggregates.

(Magnification 30,000)



Fig. 108

Electron micrograph of cellulose triacetate film dyed with Serisol Violet 2R , showing the presence of dye aggregates. (Magnification 30,000).

A P P E N D I X

(data used in Text)

TABLE

Light fastness tests of Levafix dyes on Wool

	1	2	3	4	5	6	
Templeton	6-7	4	4	4	5	6	U.F.
	6-7	4	4-5	4-5	5	6-7	F.
Bayer 71 hr.	7	5-6	6	5-6	7	7	U.F.
	7	6	6	6	6	7	F.
This laboratory 129 hr.	All faded more or less the same						U.F. F.

Note:

U.F.	=	Unfixed dyeings
F.	=	Fixed dyeing
Col. 1	=	Levafix Brilliant Yellow E-3G
" 2	=	Levafix Brilliant Scarlet E-3B
" 3	=	Sirius Light Turkish Blue GL
" 4	=	Levafix Turkish Blue E-G
" 5	=	(Levafix Brilliant Yellow E-3G (Levafix Turkish Blue E-G
" 6	=	(Levafix Brilliant Yellow E-3G (Sirius Light Turkish Blue GL

TABLE

Light fastness & Wash fastness data

Dyes	L.F.				W.F.	
	Cotton		Viscose		Cotton	Viscose
	B	W	B	W		
Procion Brill. Yellow 6G	5 6-7 6-7	5 6-7 6-7	5-6 6-7 6-7	5-6 6-7 6-7	5	5
Procion Yellow GR	5 6 6	5 5-6 6	5 6-7 6-7	5 6 6-7	5	5
Procion Yellow RS	6 6 6	6 6 6	6-7 6-7 6-7	6-7 6-7 6-7	5	4-5
Procion Brill. Orange G	4-5 5 5-6	4 4-5 5	5-6 6-7 6-7	5 6-7 6-7	4-5	4-5
Procion Brill. Orange 2BS	3 4 4-5	2 4 4	4 5 5-6	2 4 4-5	5	5
Procion Scarlet G	3-4 4 4	3 3-4 4	4 4-5 5	4 4-5 5	4	4-5
Procion Red G	3-4 4-5 5	3-4 4-5 4-5	4-5 6 6-7	4 6 6-7	5	5
Procion Brill. Red 2BS	4-5 5 5-6	4 5 5-6	5 6 6	5 6 6	5	4
Procion Brill. Red 5BS	4 4-5 4-5	3-4 4 4-5	5 6 6	5 6 6	5	5

TABLE

(Cont'd)

Dyes	L.F.				W.F.	
	Cotton		Viscose		Cotton	Viscose
	B	W	B	W		
Procion Brill. Red 8B	3-4 4-5 4-5	3-4 4 4	4 5 5-6	4 5 5-6	5	5
Procion Rubine B	6 6-7 6-7	6 6-7 6-7	6-7 6-7 7	6-7 6-7 7	5	5
Procion Red Brown 4R	3-4 4-5 5	3 4 4-5	4-5 4-5 5	4-5 4-5 5	5	5
Procion Blue 3R	3-4 5 5-6	3-4 5 5-6	4-5 5-6 6-7	5 6 6-7	5	5
Procion Brill. Blue R	6 6 6-7	6 6 6-7	6-7 6-7 6-7	6-7 6-7 6-7	5	5
Procion Blue 3G	6-7 6-7 6-7	Same	6-7 6-7 6-7	Same	4	4
Procion Grey G	4-5 5 5	4 5 6	4-5 6 6-7	5 6 6-7	5	4-5
Procion Brill. Blue H7 G	3-4 5 5-6	3-4 4-5 5	4-5 6 -	4-5 6 -	4-5	5
Procion Brill. H5 G	4 5-6 6	4-5 5-6 6	4-5 6 -	4-5 6 -	5	5

Note:

L.F. = Light fastness and W.F. = Wash fastness.

Shade depths = 1/25

B = Bombay

W = Wilmslow

1/1

2/1

TABLE

Light Fastness & Wash Fastness data

<u>Dyes</u>	<u>L.F.</u>		<u>W.F.</u>	
	<u>Cotton</u>	<u>Viscose</u>	<u>Cotton</u>	<u>Viscose</u>
Levafix Brill. Yellow E-3G	5	6	5	5
	5	6	5	5
	6	6-7	5	5
	7	7	5	5
Levafix Yellow E-RL	6	6	5	5
	6	6	5	5
	6-7	6-7	5	5
	6-7	7	5	5
Levafix Brill. Scarlet E-3B	3-4	4	5	5
	3-4	4	5	5
	3-4	4-5	5	5
	4-5	5	5	5
Levafix Brill. Red E-2B	3-4	4-5	5	5
	3-4	5	5	5
	4	5-6	5	5
	5	6	5	5
Levafix Brill. Red E-4B	4	4-5	5	5
	4-5	5	5	5
	5	5-6	5	5
	5-6	6	5	5
Levafix Red Violet E-2BL	5	5-6	5	5
	5-6	5-6	5	5
	6	6	5	5
	6	6-7	5	5
Levafix Brill. Blue E-B	6	6	5	5
	6	6	5	5
	5-6	6	5	5
	5	6	5	5
Levafix Brill. Blue E-R	6	6-7	5	5
	6	6-7	5	5
	5-6	6-7	5	5
	5-6	6-7	5	5
Levafix Dark Blue E-G	3-4	4-5	5	5
	3-4	5	5	5
	4	5-6	5	5
	5-6	6	5	5

TABLE

(Cont'd)

<u>Dyes</u>	<u>L.F.</u>		<u>W.F.</u>	
	<u>Cotton</u>	<u>Viscose</u>	<u>Cotton</u>	<u>Viscose</u>
Levafix Turquoise Blue E-G	4-5	5	5	5
	5	5-6	5	5
	5-6	6	5	5
	6	6		

Note:

First figure	=	$\frac{1}{12}$ standard depth
Second figure	=	$\frac{1}{6}$ standard depth
Third figure	=	$\frac{1}{3}$ standard depth
Fourth figure	=	Standard depth

TABLE

(Cont'd)

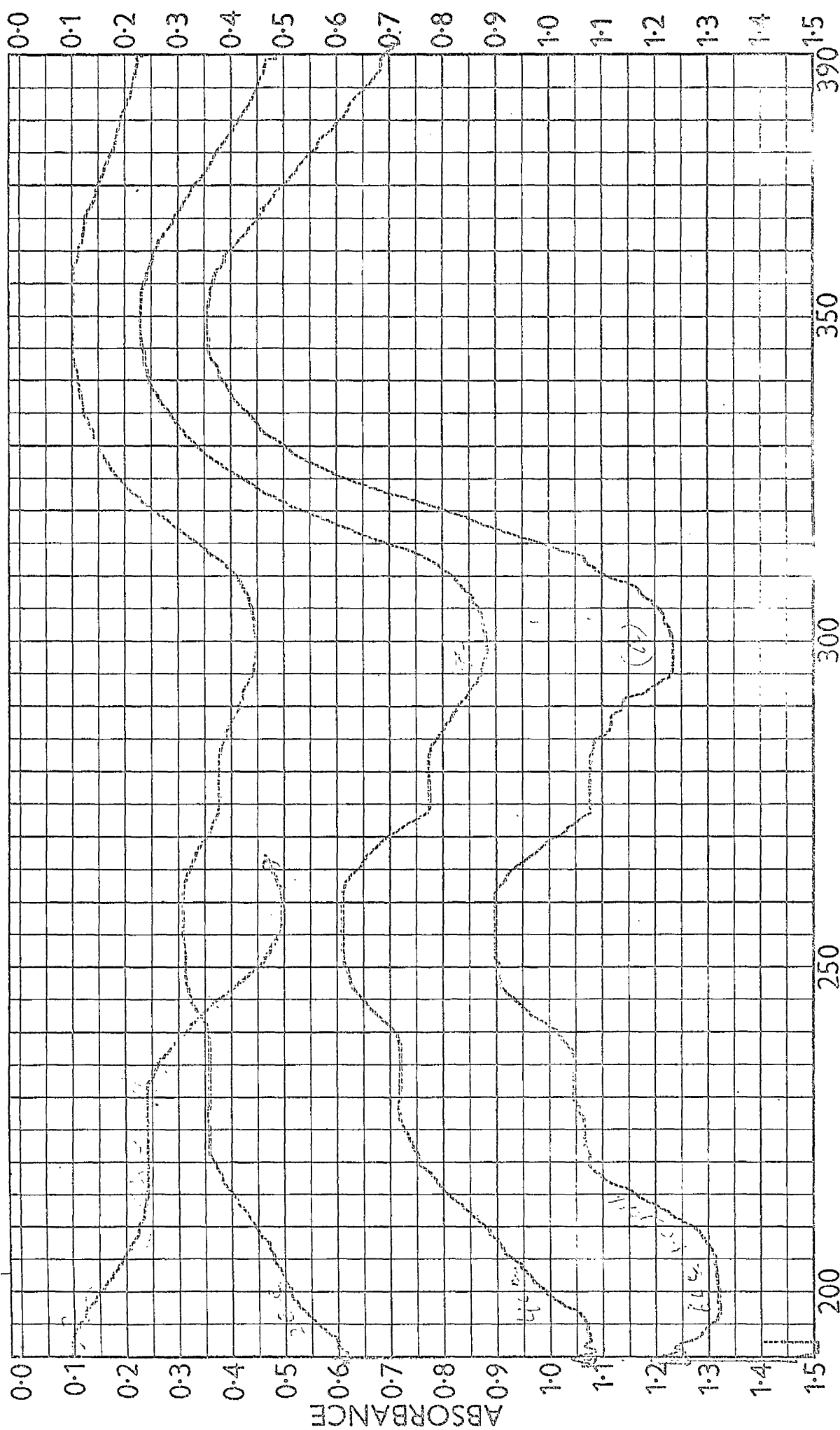
<u>Dyes</u>	<u>C</u>	<u>V</u>
Drimarene	4	4-5
Scarlet Z-GL	5-6	6
	6	6-7
Drimarene	4	4
Red Z-RL	5	5
	6	6-7

<u>Dyes</u>	<u>C</u>	<u>V</u>
Drimarene	3-4	3-4
Red Z-BL	4-5	5
	5-6	6
Drimarene	3-4	3-4
Red Z-3B	4	4-5
	5	6

Notes:

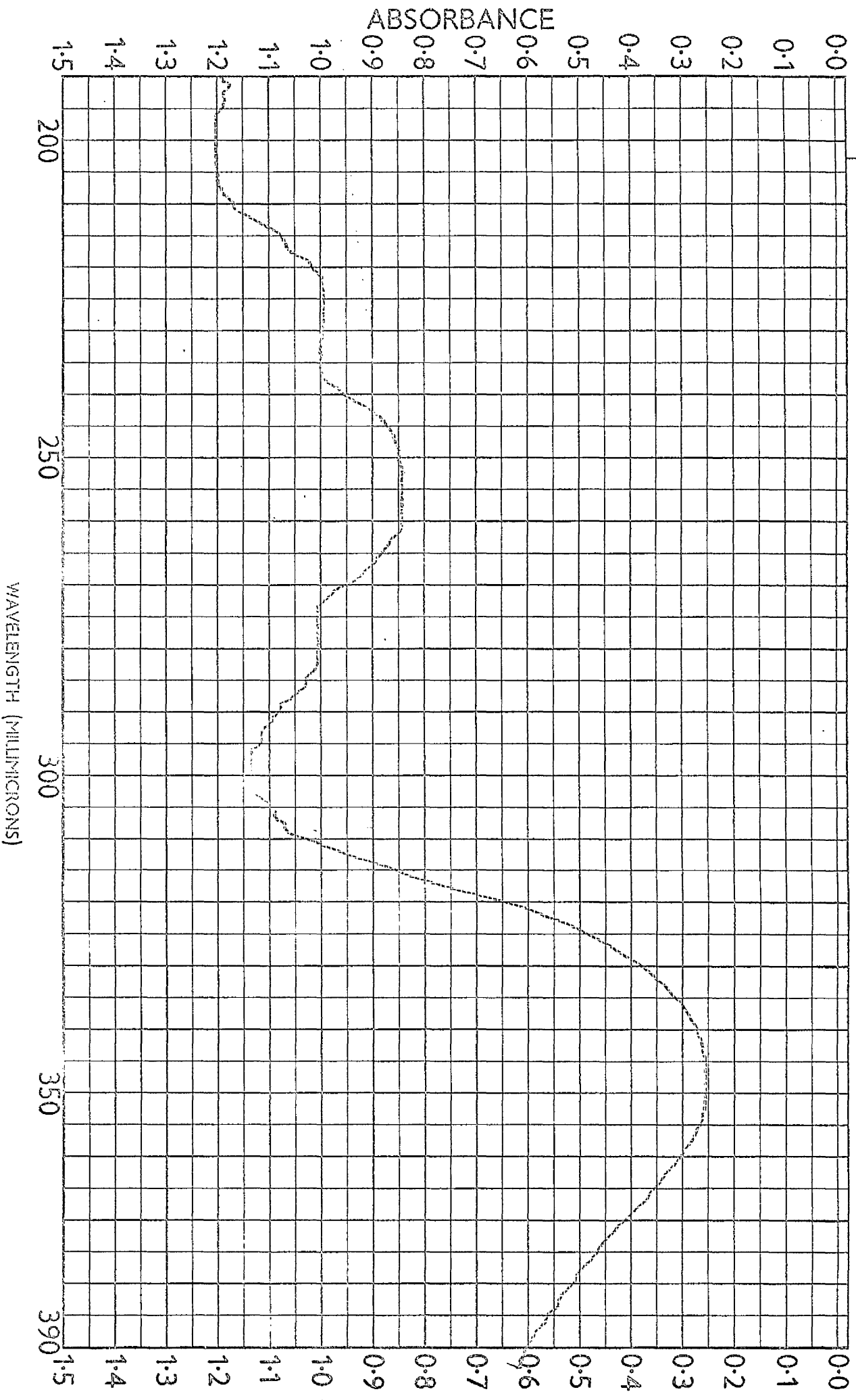
First figure = $\frac{1}{25}$
 Second figure = $\frac{1}{3}$
 Third figure = $\frac{1}{1}$

UV

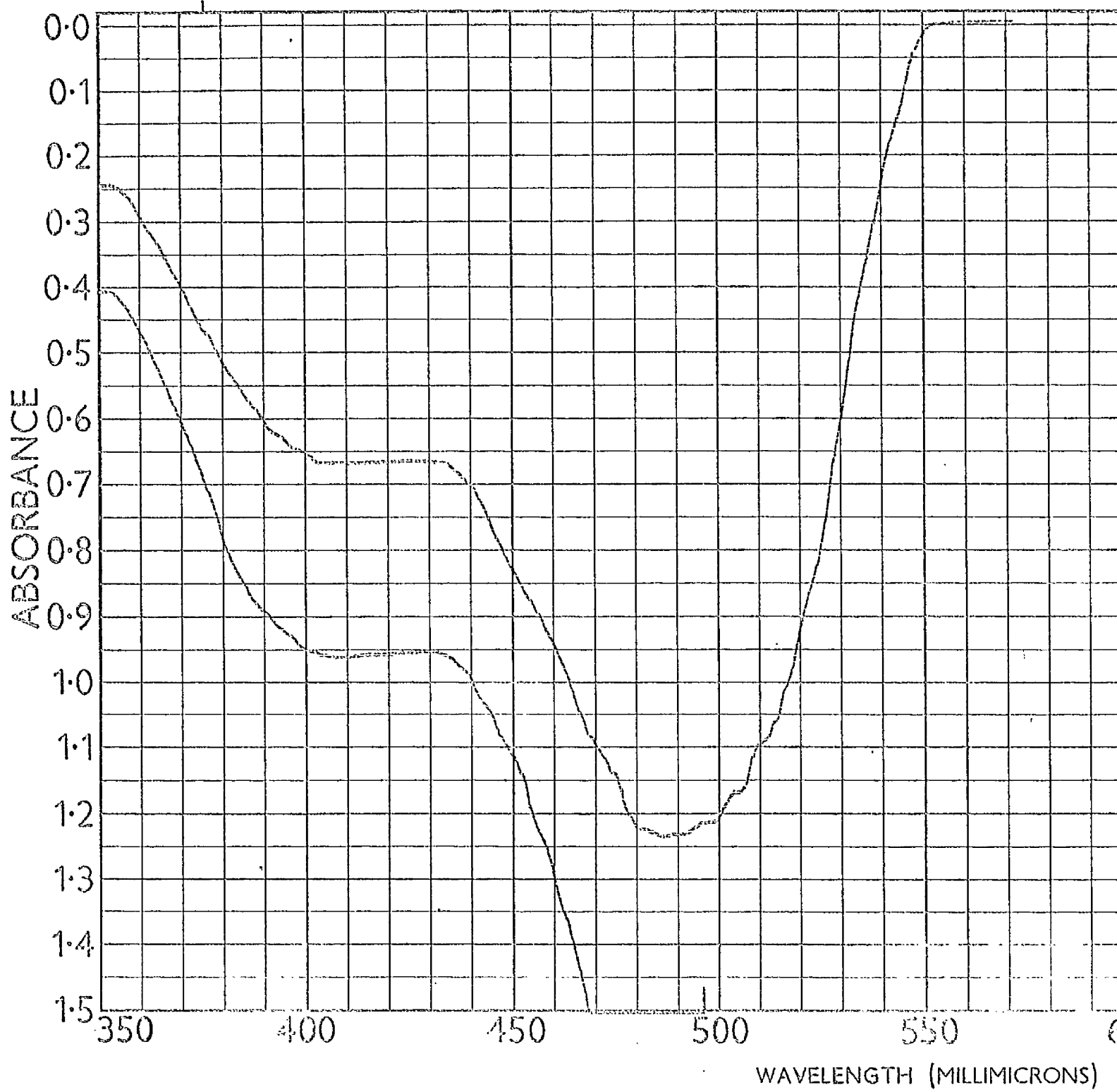


WAVELENGTH (MILLIMICRONS)

SAMPLE <u>Ac. Butylamine H₂O</u>	CURVE NO. <u>(a)</u>	SCAN SPEED <u>100</u>	OPERATOR
	CONC <u>with 10% solution of H₂O</u>	SPLIT <u>2</u>	DATE
ORIGIN <u>11.15</u>	CELL PATH	REMARKS <u>for standard 11.15</u>	

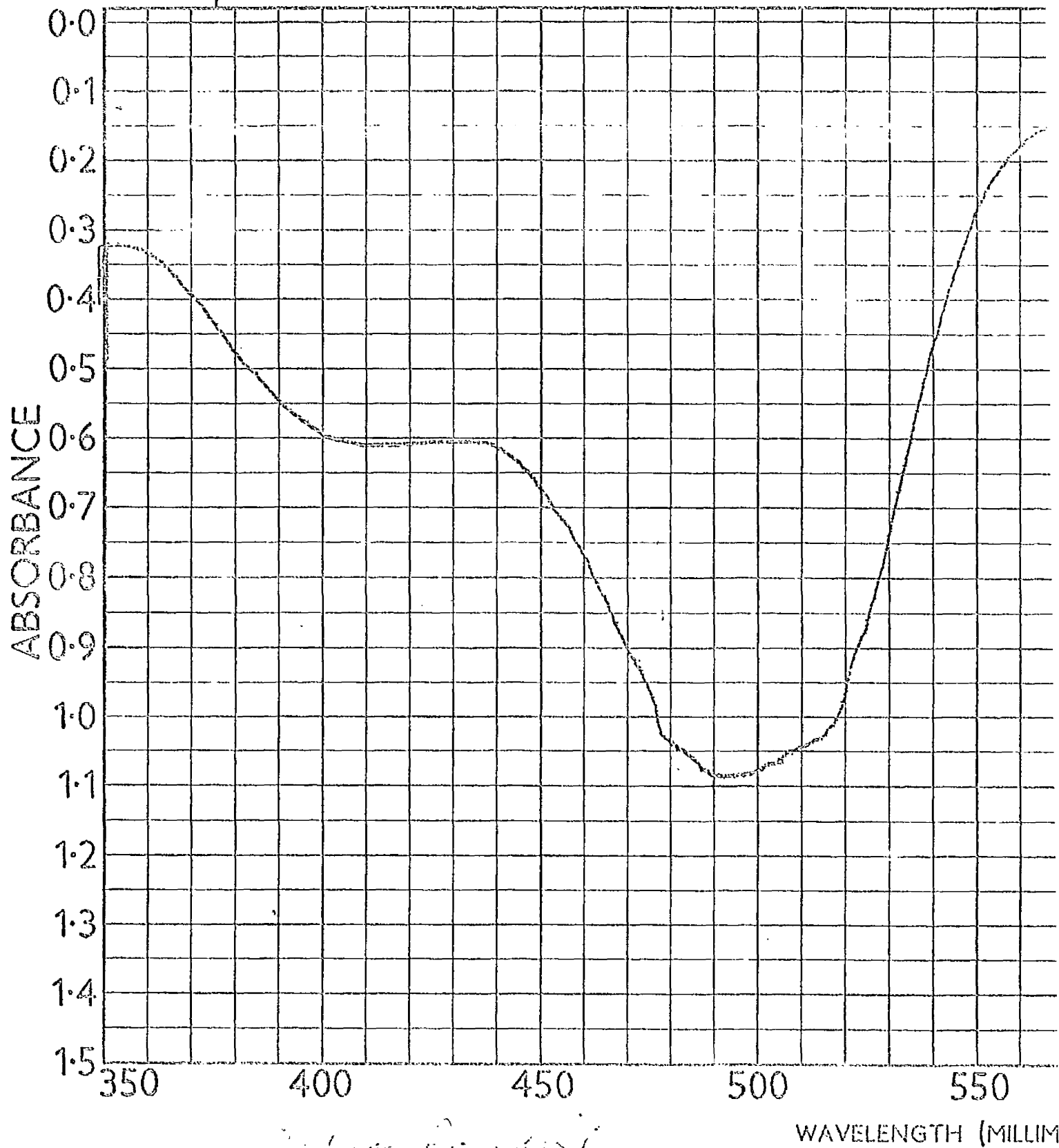


SAMPLE <u>Benz. Benzoate NCS</u>		CURVE NO. <u>11</u>		SCAN SPEED <u>10</u>		OPERATOR <u>NY</u>	
ORIGIN _____		CONC _____		SLIT _____		DATE <u>1/1/46</u>	
SOLVENT <u>100% Benz. Gr</u>		CELL PATH _____		REFERENCE _____		REMARKS _____	



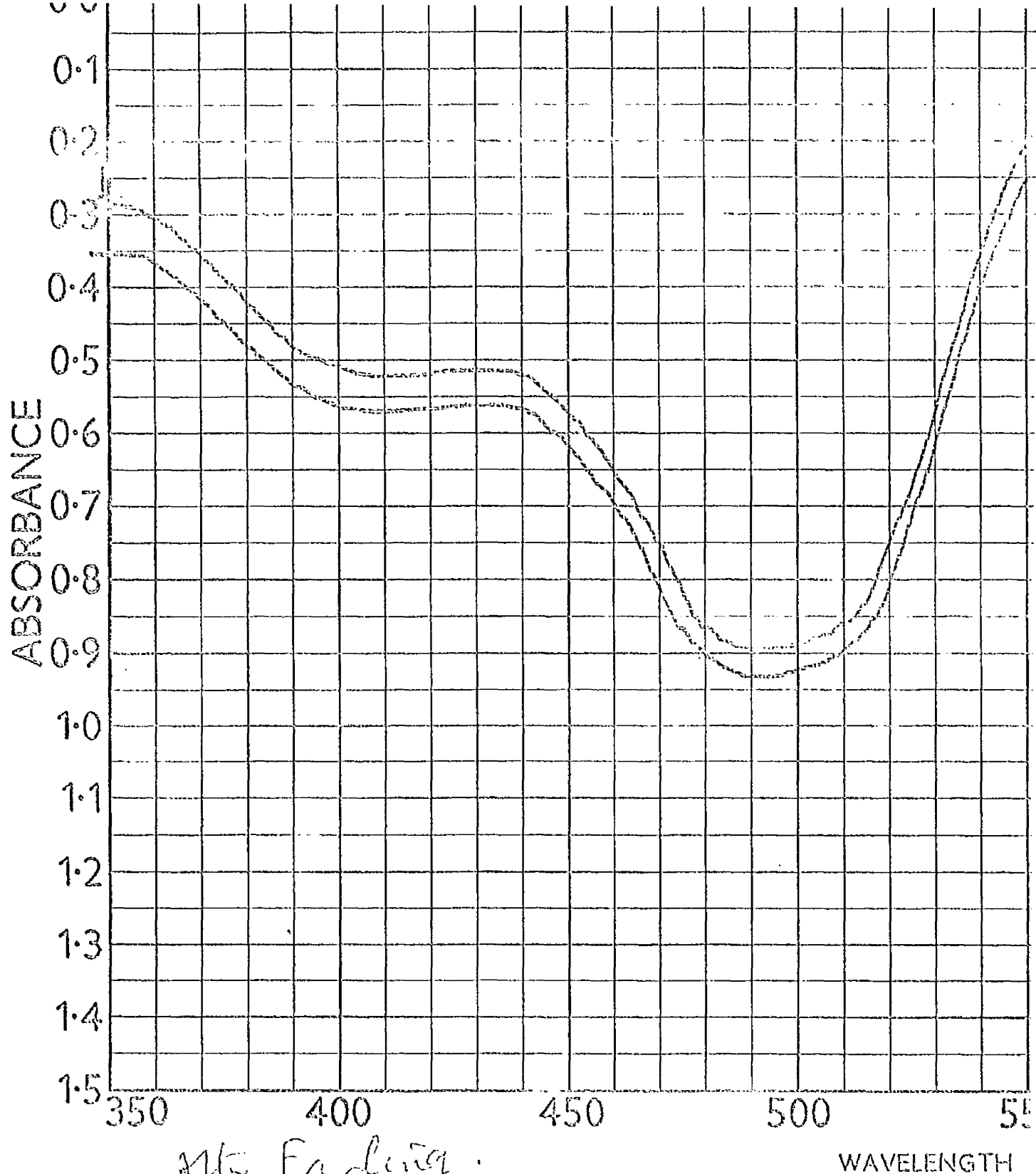
SAMPLE Pre Boiled Tap Water
ORIGIN _____
SOLVENT Tap Water

CURVE NO 11
CONC _____
CELL PATH _____
REFERENCE _____



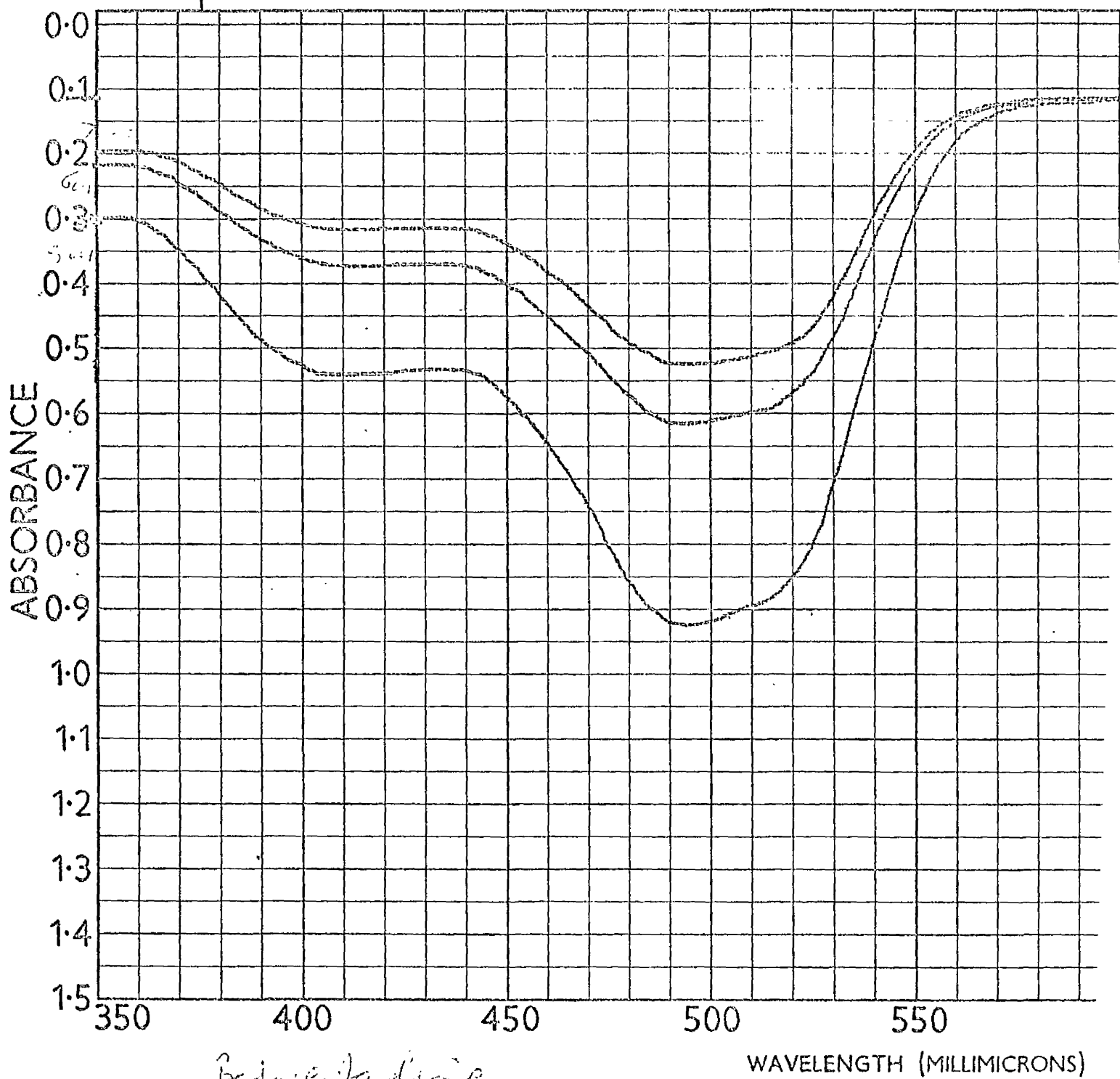
Active Pencil

SAMPLE <u>5111</u>	CURVE NO _____
<u>Active Pencil Cream MSO</u>	CONC _____
ORIGIN _____	CELL PATH _____
SOLVENT _____	REFERENCE _____



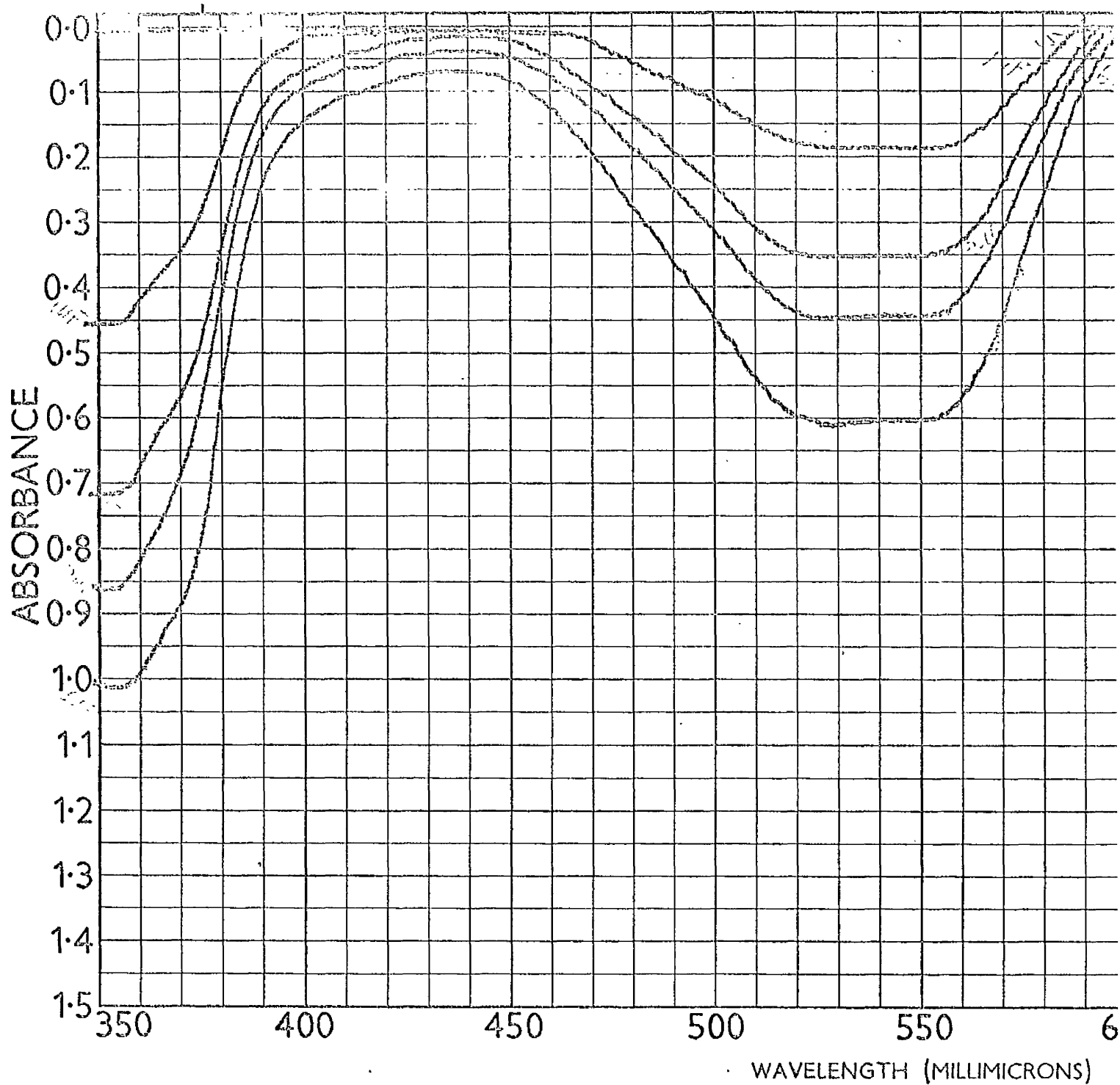
After Fading.

SAMPLE <u>5F</u>	CURVE NO <u> </u>
<u>Breion Brill Orange MS6</u>	CONC <u> </u>
ORIGIN <u> </u>	CELL PATH <u> </u>
SOLVENT <u> </u>	REFERENCE <u> </u>



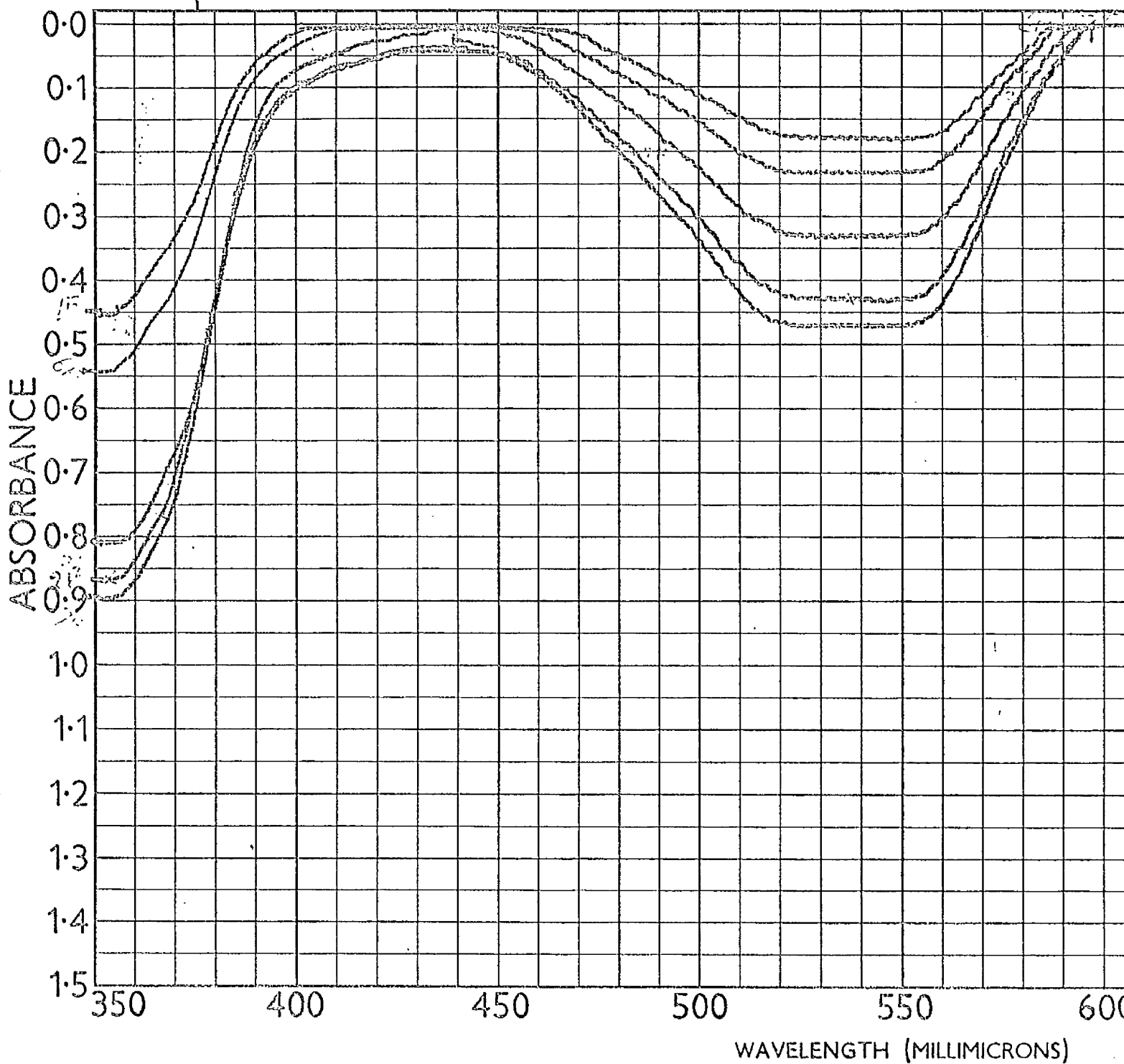
Before fading

SAMPLE <u>7UF, 6UF, 5UF</u>	CURVE NO _____
<u>Protein Bull. Lysate M5G</u>	CONC _____
ORIGIN _____	CELL PATH _____
SOLVENT _____	REFERENCE _____



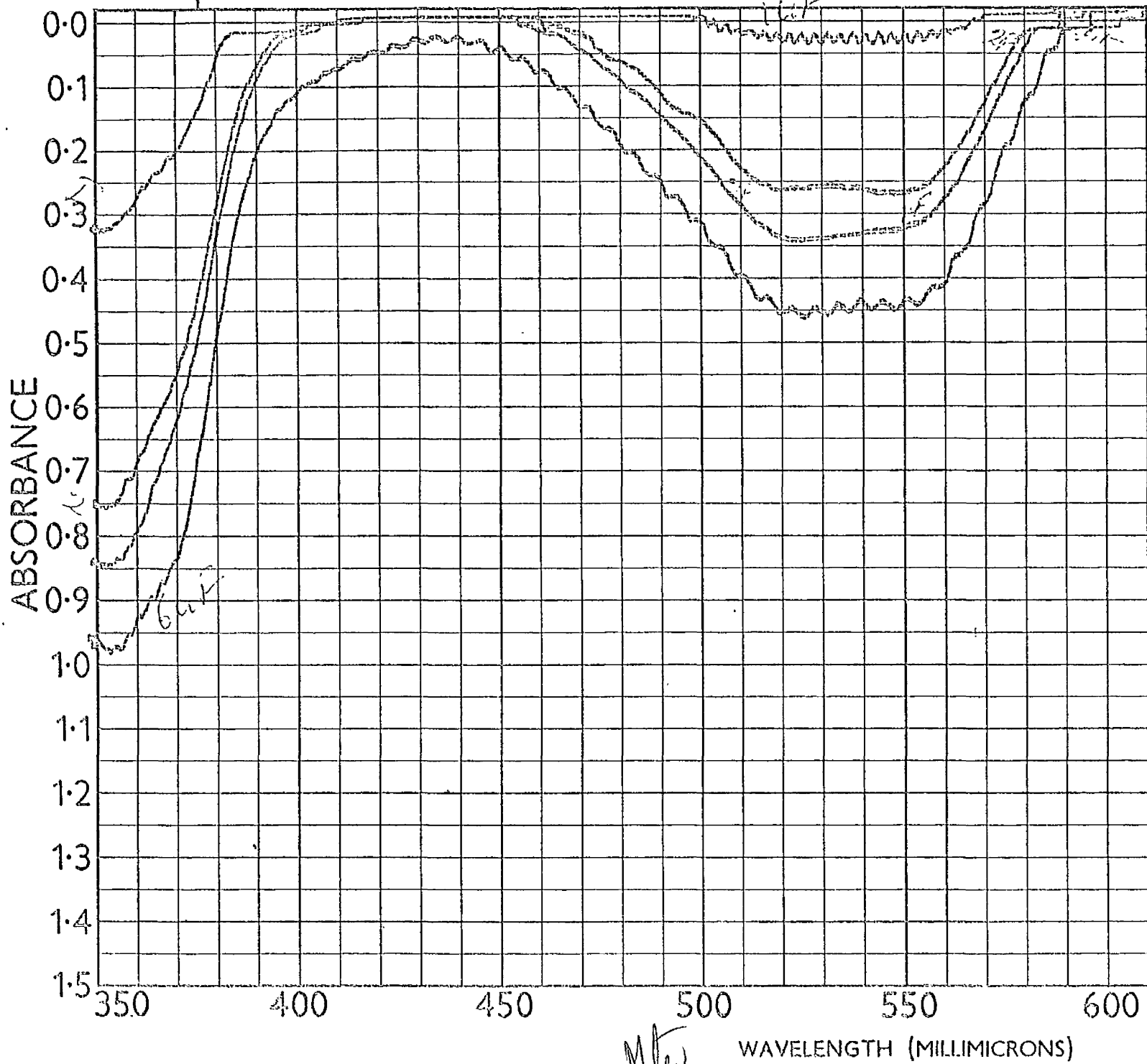
SAMPLE Dye 1000 (11F)
On Gel-Cellulose paper for
 ORIGIN 1000
 SOLVENT Dye 1000 20/3/66

CURVE NO _____
 CONC _____
 CELL PATH _____
 REFERENCE _____



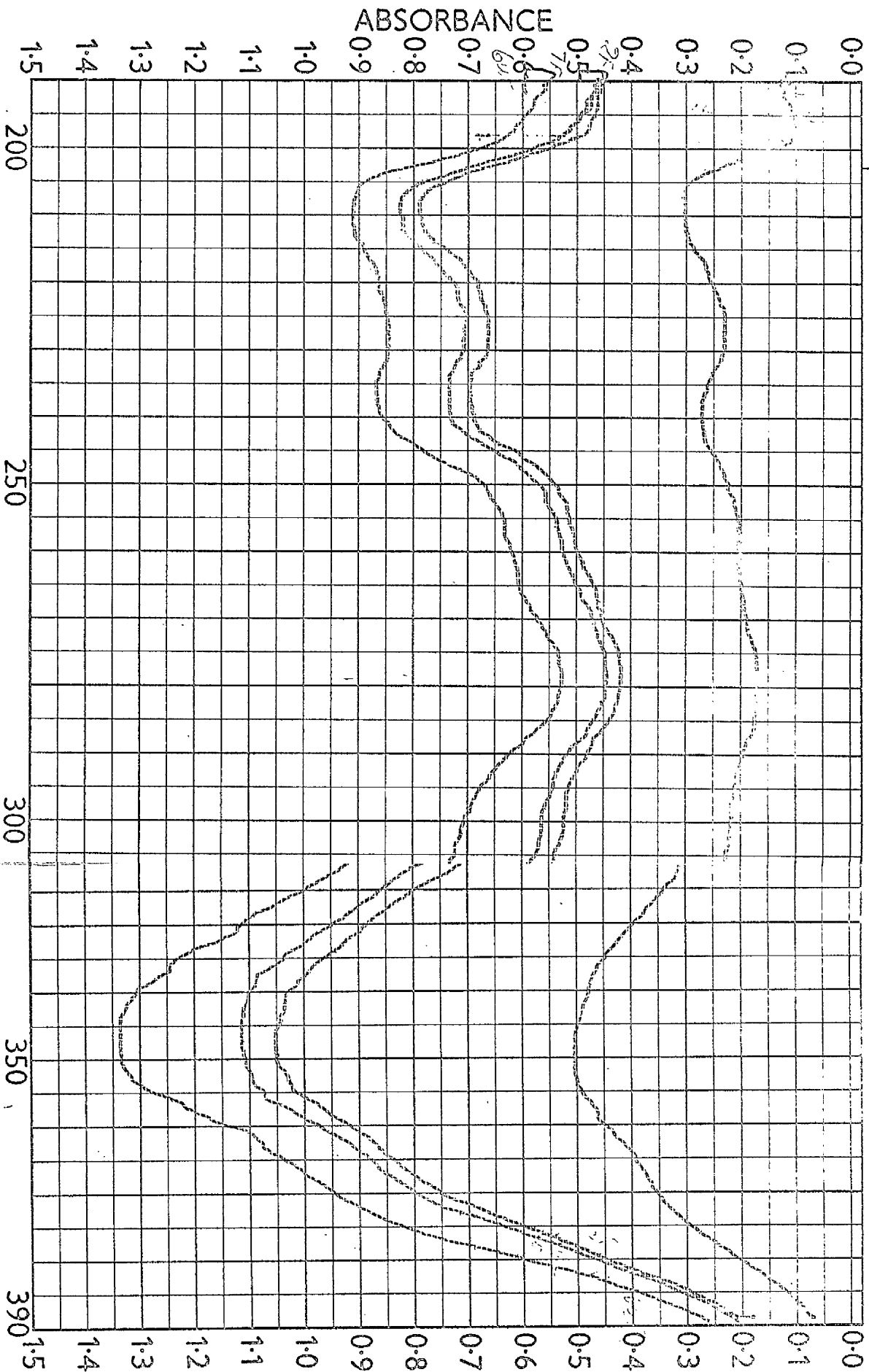
SAMPLE Dr. J. K. G. (F)
... ..
 ORIGIN ...
 SOLVENT ...

CURVE NO. _____
 CONC. _____
 CELL PATH _____
 REFERENCE _____



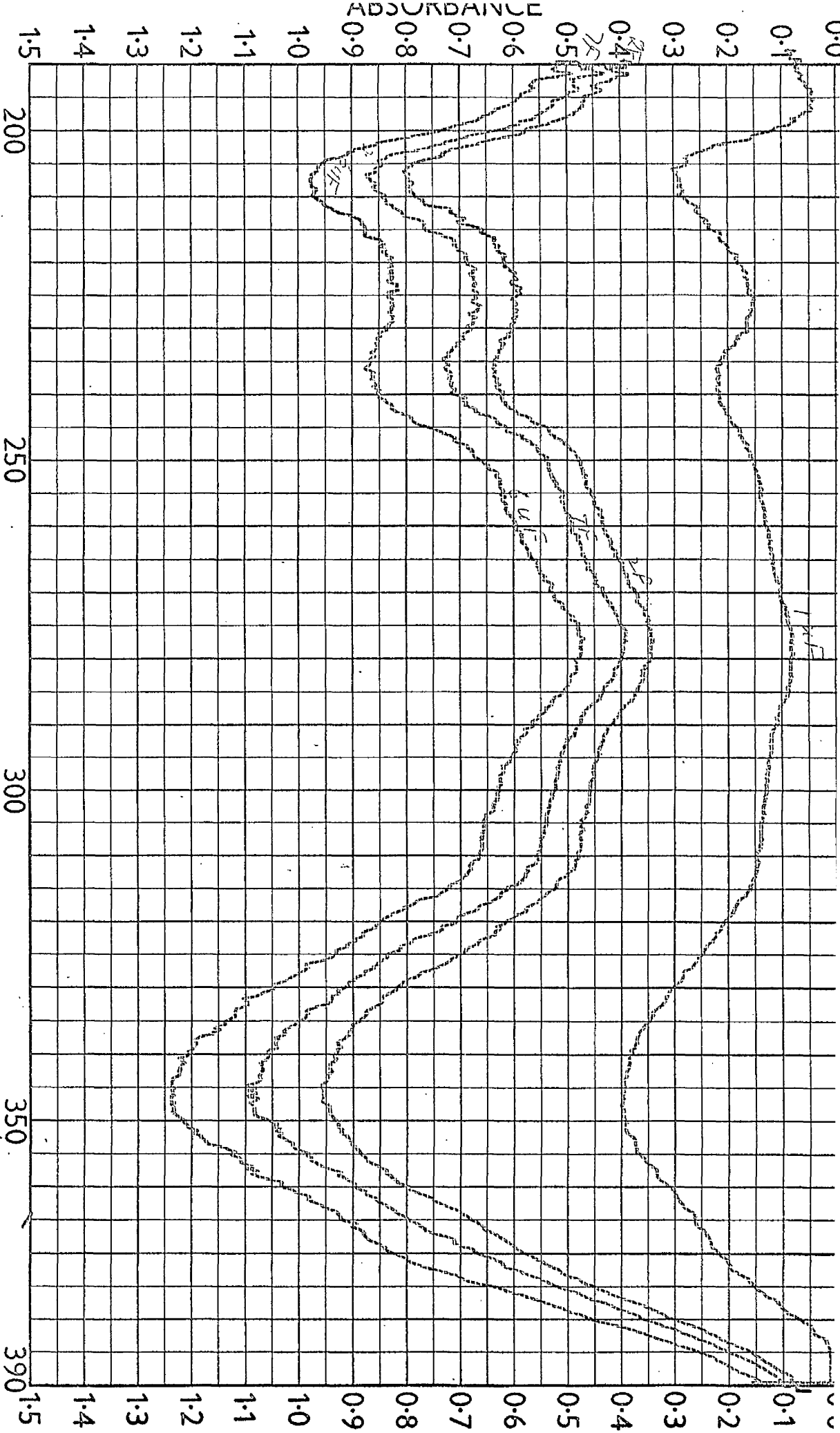
SAMPLE Direct Pink G. (F&W)
in 0.1% methanol
 ORIGIN for 100%
 SOLVENT Dye 1 in 20/3/66

CURVE NO _____
 CONC _____
 CELL PATH _____
 REFERENCE _____

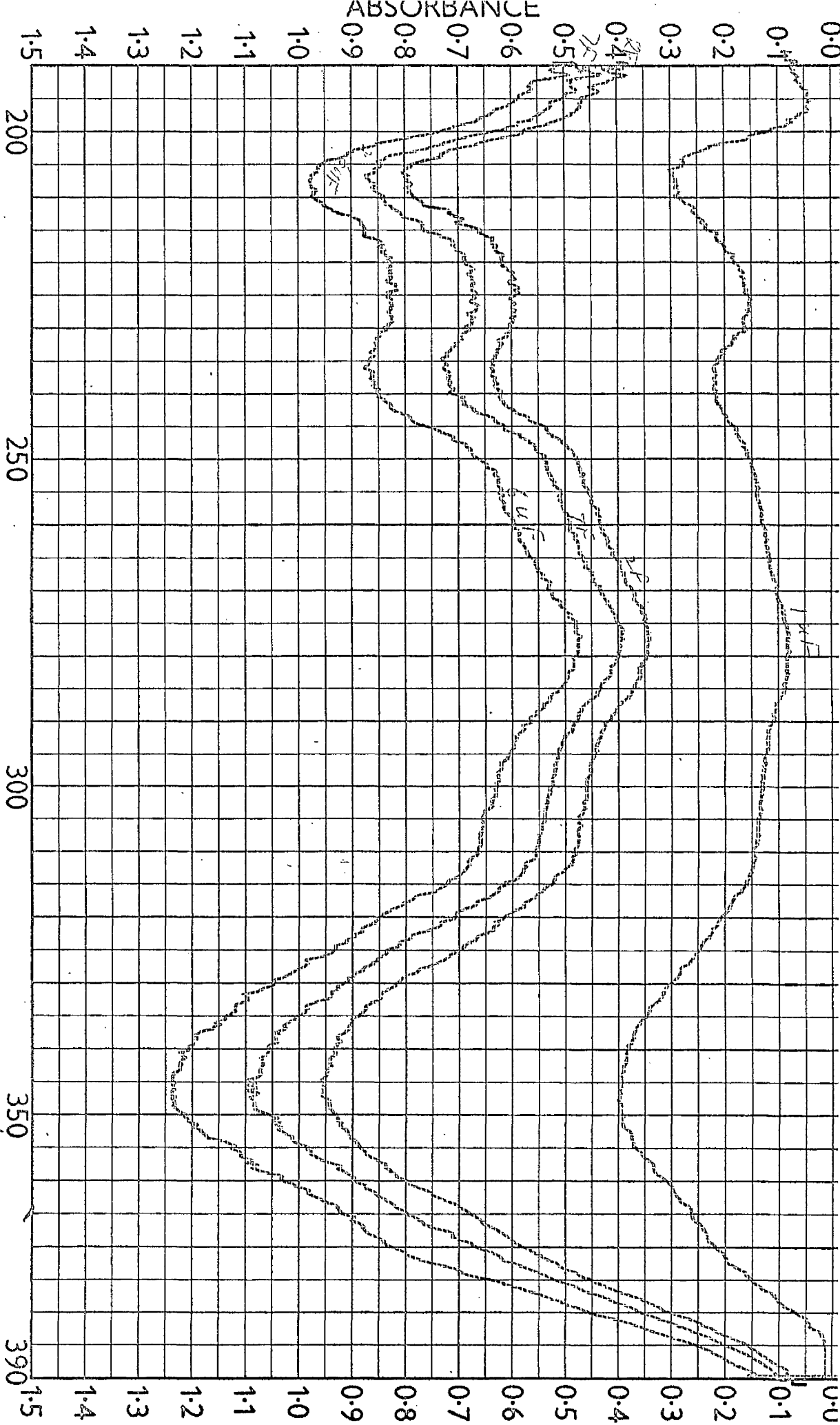


Before packing

SAMPLE <u>Direct Link G (F411F)</u>		CURVE NO. <u>1</u>	SCAN SPEED <u>Fast</u>	OPERATOR <u>Dr</u>
ORIGIN <u>En Gel - Cellulose 4-4-</u>		CONC <u>1</u>	SLOT <u>25</u>	DATE <u>1/1/66</u>
SOLVENT <u>1 Dip 96 conc 20/3/66</u>		CELL PATH <u>1</u>	REMARKS <u></u>	



SAMPLE <u>Bright Pink G (F+UE)</u>		CURVE NO. _____	SCAN SPEED <u>Fast</u>	OPERATOR <u>108</u>
ORIGIN <u>En Gd - cellulose paper</u>		CONC _____	SLIT <u>25</u>	DATE <u>2/2/66</u>
SOLVENT <u>Dye in water</u>		CELL PATH _____	REMARKS _____	



WAVELENGTH (MILLIMICRONS)

After peak

SAMPLE <u>brick Pink G (F44F)</u>		CURVE NO. _____	SCAN SPEED <u>fast</u>	OPERATOR <u>10/</u>
ORIGIN <u>8. Gel - cellulosane paper</u>		CONC _____	SPLIT <u>25</u>	DATE <u>29/2/66</u>
SOLVENT <u>1 Dye solvent 3/66</u>		CELL PATH _____	REMARKS _____	
		REFERENCE _____		